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The Use of Lime in the Treatment of Municipal Wastewaters

Research Report No. 21



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**Research Program for the Abatement of Municipal Pollution
under Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality**

Research Report No. 21 Use of Lime in the Treatment of Municipal Wastewaters

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These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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of municipal wastewaters /
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THE USE OF LIME IN THE TREATMENT
OF MUNICIPAL WASTEWATERS

by

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RESEARCH PROGRAM FOR THE ABATEMENT
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AGREEMENT ON GREAT LAKES WATER QUALITY

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ABSTRACT

The primary objective of this investigation was to develop a process for treating municipal wastewaters based on the addition of lime. The principal parameters studied were the removal of phosphorus, suspended solids, COD, BOD, and microorganisms in order to produce an effluent suitable for discharge, with or without subsequent treatment. The addition of magnesium and/or iron salts was also studied to determine if phosphorus removal could be improved.

Experimental results indicated that, at pH 11.5 in hard water areas with a magnesium content of >10 mg/l, magnesium had no appreciable beneficial effect. In waters of lower magnesium content, (<5 mg/l), the addition of magnesium improved the general effluent quality, but not the phosphorus removal.

Consequently, all effluent characteristics were monitored to determine the effect of lime treatment with and without supplemental magnesium on the removal of undesirable impurities. In general, the addition of lime to pH 10.0 removed most of the phosphates, but produced a low quality effluent with regard to other characteristics. Addition of lime to pH 11.0 and 11.5 produced effluents of considerably improved quality. At pH 11.5, phosphates were reduced by 98%; turbidity also was reduced by 98%; BOD and COD reduction averaged 74% and 67% respectively; suspended solids were reduced by 80%; and total coliforms were totally and consistently eliminated (from approximately 2×10^6 /100 ml to zero in nine jar test trials). It was therefore probable that this effluent, if produced under optimal conditions, was of sufficient quality to be discharged to most Canadian bodies of water.

Where further purification is desired, air stripping for ammonia removal and treatment with activated carbon, or ozone could be employed for further BOD reduction. It should be pointed out that existing

* The average residual values after treatment were:

Phosphates	0.2 mg/l @ 98% removal	raw level	10 mg/l
BOD	15 mg/l @ 74%	" "	58 "
COD	36 mg/l @ 67%	" "	110 "
Suspended Solids	17 mg/l @ 80%	" "	85 "

primary treatment facilities can be readily converted to a lime treatment system with some modifications as suggested in the report.

Preliminary calcination studies on the lime sludge indicated that the absorbed organic material can be incinerated and a good quality lime produced (Appendix A). Settling tests were carried out to provide data for sizing clarifiers, and sludge weight, volume, and alkalinity were considered in the preliminary design of a full scale treatment system for a small town.

A literature review on the use of lime in the treatment of wastewaters is presented as an appendix to this report. A supplemental reference list has also been included for those seeking information on specific topics concerning the use of lime.

RÉSUMÉ

Le but premier de la présente étude était de mettre au point un procédé d'épuration des eaux usées municipales reposant sur une addition de chaux. Les principaux paramètres qu'on a étudiés ont été l'élimination du phosphore, des matières en suspension, de la DCO, de la DBO et des microorganismes afin d'obtenir un effluent qu'on pourrait évacuer avec ou sans traitement ultérieur. On a aussi étudié l'addition de sels de magnésium et/ou de fer pour savoir si l'élimination du phosphore pouvait voir son rendement accru.

Les résultats ont montré que le magnésium à pH de 11.5 n'avait pas d'effet positif appréciable dans les régions où l'eau était dure et avait une teneur en magnésium supérieur à 10 mg/l. Dans les eaux où cette teneur était plus faible (< 5 mg/l), l'addition de magnésium a eu pour effet d'améliorer la qualité générale de l'effluent mais non pas le rendement de l'élimination du phosphore.

Par conséquent, on a surveillé toutes les caractéristiques de l'effluent afin de déterminer l'action du traitement à la chaux, avec ou sans magnésium complémentaire, sur l'élimination des impuretés indésirables. De façon générale, l'addition de chaux à pH de 10.0 a permis l'élimination de la plupart des phosphates mais a donné un effluent de qualité inférieur en ce qui a trait aux autres caractéristiques étudiées. À pH 11.0 et de 11.5, l'addition de chaux a donné des effluents d'une qualité hautement améliorée. A pH 11.5, les phosphates ont été réduits de 98 p. 100*; la turbidité a aussi connu le même sort; la réduction de la DBO et la DCO a été de 74 et de 67 p. 100 respectivement, en moyenne; celle des matières en suspension, de 80 p. 100 et celle des coliformes totaux, uniformément

* Les concentrations résiduelles moyennes après le traitement sont:

pour les phosphates,	0.2 mg/l	pour un rendement de 98% sur une concentration brute de 10 mg/l
pour le DBO,	15 mg/l	pour un rendement de 74% sur une concentration brute de 58 mg/l
pour le DCO,	36 mg/l	pour un rendement de 67% sur une concentration brute de 110 mg/l
pour les matières en suspension,	17 mg/l	pour un rendement de 80% sur une concentration brute de 85 mg/l

et constamment totale (à partir de $2 \times 10^6/100$ ml jusqu'à zéro au cour de test en éprouvette). La qualité de cet effluent (obtenue aux conditions optimales) était donc suffisante pour permettre son déversement dans la plupart des masses d'eau au Canada.

Pour une meilleure épuration, on pourrait recourir à l'entraînement de l'ammoniac par l'air, et au charbon actif ou à l'ozone pour la réduction plus efficace de la DBO. Il est à noter que les installations de traitement primaire actuelles peuvent être facilement transformées en un système d'épuration à la chaux suite à certaines modifications suggérées dans le rapport.

Des études préliminaires sur l'incinération de la boue de chaux ont indiqué qu'on peut incinérer la matière organique absorbée et produire une chaux de bonne qualité (Annexe A). On a fait des tests de sédimentation pour obtenir des données permettant l'établissement des paramètres opérationnels des clarificateurs et on a tenu compte du poids, du volume et de l'alcalinité des boues pour la conception provisoire d'un système d'épuration grandeur nature des eaux d'une petite municipalité.

En annexe de ce rapport, on trouvera un exposé documentaire traitant de l'utilisation de la chaux dans l'épuration des eaux usées. Pour ceux qui veulent obtenir des renseignements sur des sujets particuliers concernant l'utilisation de la chaux, on a ajouté une liste de références.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
TABLE OF CONTENTS	v
List of Figures	vii
List of Tables	ix
1. SUMMARY AND CONCLUSIONS	1
1.1 A Concept for Lime Treatment of Wastewater	1
1.2 Condensed Literature Review	3
1.3 Conclusions	8
2. PROCESS SELECTION AND DESCRIPTION	10
3. EXPERIMENTAL	15
3.1 Remarks	15
3.2 Pincourt Wastewater Study	15
3.3 Effect of pH on a Weak Effluent	15
3.4 The Effect of Magnesium on a Weak Effluent	19
3.5 Beaconsfield Wastewater Study	19
3.6 Effect of Magnesium on a Stronger Effluent	21
3.7 Variability in Strength of Beaconsfield Wastewater	21
3.8 Supplemental Phosphorus Addition to Combination of Lime and Magnesium Treatment	21
3.9 Low pH Treatment of Wastewater with and without Magnesium and with and without Sludge Recycle	23
3.10 Effluent Quality as a Function of pH and Recycle	23
3.11 pH and Bacterial Numbers	26
3.12 Iron Salts in Lime Treated Wastewaters	29
3.13 Effect of Duration of Stirring on Effluent Quality	29
3.14 High pH Treatment on Low Magnesium Waters	32
3.15 Heavy Metal Removal at High pH	36
3.16 Post Carbonation Precipitation	38
3.17 Studies at Red Rock - A Soft Water Area	41
3.17.1 Effect of pH on Red Rock Wastewater Quality	41
3.17.2 Effect of Various Magnesium Levels on Red Rock Effluent at pH 11.5	43
3.17.3 Relation Between Duration and Rapid Mixing and Settling Rates	46
3.17.4 Settling Tests for Clarifier Design	46
4. CONCLUSIONS	50
ACKNOWLEDGEMENT	52
REFERENCES	53

TABLE OF CONTENTS (CONT'D)

	<u>Page</u>
APPENDIX A - PRELIMINARY CALCINATION STUDIES OF LIME SLUDGE FROM WASTEWATER TREATMENTS	57
APPENDIX B - pH RESPONSE TO LIME ADDITION - PINCOURT, BEACONSFIELD AND RED ROCK WASTEWATER	63
APPENDIX C - LIME TREATMENT OF MUNICIPAL WASTEWATERS - A LITERATURE REVIEW	69

LIST OF FIGURES

<u>FIGURE</u>		<u>Page</u>
1	Flow Diagram of a Physical-Chemical Treatment System	6
2	Removal Efficiencies - Physical-Chemical Treatment - Blue Plains Pilot Plant	7
3	Proposed Lime Treatment Systems	12
4	Effect of pH on Magnesium Level in Supernatant	18
5	Residual PO ₄ in Supernatant and Total Settled Solids as a Function of pH in Beaconsfield Municipal Sewage	28
6	Beaconsfield Municipal Effluent - Effect of pH on Survival of Bacteria in Lime Treated Sewage.	30
7	Effect of Stir Time on Suspended Solids and Turbidity	34
8	Interdependency of Sludge Volume, Suspended Solids, pH, and Coagulant Aid	44
<u>Appendix B</u>		
B1	Pincourt - pH Response of Raw Sewage to Lime Addition	64
B2	Beaconsfield - pH Response of Raw Sewage to Lime Addition	65
B3	Red Rock - pH Response to Lime Addition	66
<u>Appendix C</u>		
C1	The Lime Dose for pH \geq 11.0 as a Function of Wastewater Alkalinity	72
C2	Alkalinity, Lime Dose and pH	73
C3	Lime Precipitation and Phosphorus Removal from Raw Wastewater	74
C4	Lime Precipitation and Calcium and Magnesium Concentrations in Raw Wastewater	76
C5	Chemical-Biological Systems	86

LIST OF FIGURES (CONT'D)

<u>FIGURE</u>		<u>Page</u>
C6	Schematic Drawing of Proposed Wastewater Treatment System	87
C7	The Effect of pH on Phosphate Removal	92
C8	Calcium and Magnesium Concentrations During a Metaphosphate Removal	95
C9	pH as a Function of Lime Dose and Alkalinity	112
C10	Lime Dose Required for pH 11.0 in Wastewaters of Various Alkalinity	113

LIST OF TABLES

<u>TABLE</u>		<u>Page</u>
1	Full Scale Plants Utilizing Chemical Treatment	4
2	Reported Wastewater Improvement Using Lime Treatment Alone or in Combination with either Biological or Chemical Treatment	11
3	Some Properties of Wastewater Used in Lime Treatment Studies	16
4	Effect of Adding Lime in Pincourt Wastewater to Various pH Levels with & without the addition of Magnesium	17
5	The Effect of High pH and Various Mg^{++} Levels on Pincourt Effluent Characteristics	20
6	The Effect of High pH and Various Mg^{++} Levels on A Strong Effluent	22
7	Phosphorus Removal at pH 11.5 in Wastewaters Supplemented with Phosphate with and without Magnesium Addition	24
8	Low pH Treatment of Beaconsfield Effluent with and without Magnesium, with and without Iron Salts, with and without Sludge Recycle	25
9	Beaconsfield Effluent Quality as a Function of pH and Sludge Recycle	27
10	Effect of High pH and Iron Addition at Various Points on the Quality of Beaconsfield Effluent	31
11	Effect of Stirring Time on the Quality of Beaconsfield Effluent Adjusted to pH 11.5	33
12	Effect of Rapid and Slow Stirring Time on Sludge Volume and Turbidity on Beaconsfield Effluent	35
13	Effect of High pH with and without Magnesium Supplements in Treatment of Soft Ottawa City Wastewater	37
14	Effect of High pH on Heavy Metal Removal in Beaconsfield Wastewater	39
15	Amount of $PO_4 -P$ in Post Carbonation Precipitation After 18 Hours	40
16	Effect of pH and Mg^{++} on Wastewater Treatment 11.5 (Red Rock)	42

LIST OF TABLES (CONT'D)

<u>TABLE</u>		<u>Page</u>
17	Effect of Mg^{++} in Wastewater Treatment at pH 11.5 (Red Rock)	45
18	Effect of Rapid Stirring on Settling Rate (Red Rock)	47
19	Clarifier Performance Data Derived from Settling Tests	48

APPENDIX C

C1	Effect of Magnesium on Lime Clarification	78
C2	A Comparison of Trickling Filter-Tertiary Performance with the Existing Willow Lake STP Final Effluent	79
C3	Solubility Products of Cationic Heavy Metal Oxides or Hydroxides	81
C4	Lime Coagulation and Recarbonation	82
C5	Regulatory Agency Requirements	84
C6	Design Parameters for Municipal Wastewater Treatment Plants Using Lime Clarification and Carbon Adsorption	88
C7	Effect of Lime Treatment	89
C8	Estimated Capital and Operating Costs for 1, 10 and 100 MGD Lime Clarification and Carbon Adsorption Municipal Wastewater	90
C9	Estimated Capital Costs for a 10 MGD Conventional Activated Sludge Treatment Plant with Sludge Disposal by Thickening, Filtration and Incineration	91
C10	pH, Alkalinity, and Lime Dose Relationships	111

1 SUMMARY AND CONCLUSIONS

1.1 A Concept for Lime Treatment of Wastewater

The current requirement for phosphorus removal from wastewaters in the Great Lakes Watershed has focused attention on the use of lime in sewage treatment systems. A substantial body of literature has been published on various methods of lime treatment:

- a) As a high pH tertiary stage, following primary and secondary treatment (Lake Tahoe). (1)
- b) As a high pH primary treatment prior to carbon adsorption (Blue Plains pilot plant, Washington, D.C.). (2)
- c) As a medium pH primary treatment followed by biological treatment (Newmarket, Ontario). (3)

In most of the above studies, the lime treatment has been one of several stages.

The results of the present study and of other studies published in the literature show that a single stage high pH treatment (pH 11.0 to 11.5) followed by clarification and subsequent pH adjustment by carbonation will not only reduce phosphorus to exceedingly low levels (usually less than 0.1 mg/l) but will also result in an effluent quality superior in important properties to that obtained by conventional primary treatment.

The treated water is markedly reduced in total bacteria (both pathogenic and benign) and is essentially free of coliforms. This lime disinfected effluent is of a sanitary quality exceeding most chlorinated primary effluents, and as such, does not require further disinfection by chlorination. In this connection, it should be noted that chlorination in conventional treatment systems results in the formation of highly toxic chloramine by reaction with the ammonia normally present.

Fetterolf (4) has shown that chlorinated municipal wastewaters after primary and secondary treatment must be diluted at least 40 to 50 fold to obtain 96 hour fish survival.

The high pH treatment also removes most heavy metal ions such as copper, cadmium, nickel, etc. which may also originate from industrial wastewaters. (5)

Although not experimentally investigated in this study, it has been shown elsewhere that ammonia can be effectively stripped from the highly alkaline wastewater prior to carbonation. Based on the quality of the receiving waters, this stripping operation may or may not be necessary.

The high lime pH treatment will precipitate, absorb and occlude organic components to an extent which results in a 50% to 80% reduction in BOD. (This high reduction is obtained in wastewaters of normal strength but the percentage reduction decreases with decreasing influent strength.) Should the remaining 20% to 50% BOD significantly reduce the dissolved oxygen in the receiving waters, then an additional treatment could be added, for example with activated carbon or ozone or an oxidation pond.

The apparent absence of odour in this process and the much smaller land requirements could be definite advantages in the selection of a plant location, as compared with conventional primary and secondary treatment systems.

Equipment requirements include lime storage, handling and mixing facilities, together with two clarifiers.

Treatment of the high pH effluent with carbon dioxide reduced the alkalinity and produced a precipitate of pure CaCO_3 which required clarification. The size of the clarifier can be somewhat smaller than that used for conventional primary settling because of the high settling rates of the lime sludge. The sludge volume varied from 0.5% - 1.0% of the total effluent while the corresponding solids in the sludge varied from 4.8% to 3.5%. This sludge dewatered readily on a filter leaf to 26% solids. A few preliminary experiments indicated that the carbonation could be carried out subsequent to liming but prior to clarification, resulting in the need of only one clarifier. This method needs further study.

Since the sludge is essentially odour and coliform free, it might be acceptable from an aesthetic and sanitary point of view for use as land fill without further treatment. The sludge could be more profitably used in agriculture for combined neutralization of acidic

soils and fertilization. In larger treatment plants, it may be economically attractive to calcine the lime sludge. This has the advantage of easy sludge disposal, of producing carbon dioxide for carbonation in pH adjustment, and of regenerating fresh calcium oxide from the waste, thus reducing the amount of materials in and out of the plant. In small plants without lime calcination, neutralization could be obtained by using the exhaust gases from turbines used in pumping, or by the use of purchased CO_2 , or by using sulphuric acid.

The cost of treatment would vary from plant to plant, depending on the size, the water composition, and local chemical costs. The quantity of lime required is predominantly dependent on the bicarbonate content of the water, with the lime addition as $\text{Ca}(\text{OH})_2$, varying from 200 to 500 mg/l. At this dosage, the cost would be of the order of 3¢ to 4¢ per 1000 gal if "quick lime" (CaO) is used, and approximately twice that cost if "hydrated lime" ($\text{Ca}(\text{OH})_2$) is used. Cost estimates developed at the Blue Plains pilot plant indicate that the cost, including amortization, of a combined lime and carbon treatment plant is approximately the same as that for a conventional primary and secondary sewage treatment system, i.e. approximately 22¢ per 1000 gal for a 10 mgd plant. In the Blue Plains plant, lime treatment accounted for removal of 83% of the BOD and this involved 50% of the total treatment cost. The subsequent filtration and carbon treatment brought the total BOD reduction to 94%. In some cases, depending upon the quality and volume of the receiving waters, the highest quality effluent might not be required in which case the effluent quality of the lime stage alone would suffice.

1.2 Condensed Literature Review*

At least twenty full scale chemical treatment plants are in operation or are under construction for the removal of phosphorus, suspended solids, and BOD. (Table 1.) The treatment systems will vary in the choice of chemicals (lime, alum or iron) and the stage of addition (primary, secondary or tertiary) depending upon the phosphorus level, sludge handling and disposal facilities, the wastewater hardness and alkalinity, chemical costs, and regional effluent standards.

* An extensive literature review is contained in Appendix C.

TABLE 1

Full-Scale Plants
Utilizing Chemical Treatment

<u>Primary Treatment</u>	<u>Flow</u> <u>MGD</u>	<u>Chemical</u>	<u>Status</u>
Detroit, Michigan	600	Iron	Design
Rochester, New York	100	Lime	Const.
Bay City, Michigan	12	Iron	Const.
Cleveland, Ohio	10	Iron	Design
Painesville, Ohio	5	Iron	Design
Hatfield Township, Pa.	5	Lime	Design
Holland, Michigan	4	Lime	Const.
Wyoming, Michigan	4	Iron	Design
Mentor, Ohio	2	Iron	On-Stream
<u>Mineral Addition to Aerator</u>			
Chicago, Illinois	30	Iron	Design
Seattle, Washington	20	Iron & Alum	Design
Pomona, California*	2	Alum. & Sod.Al.	Completed
Xenia, Ohio*	1	Alum.	Completed
Manassas, Virginia*	1	Alum. & Sod.Al.	Completed
Texas City, Texas*	1	Iron & Alum.	Completed
<u>Tertiary Treatment</u>			
South Lake Tahoe, Calif.	7.5	Lime	On-Stream
Manville, New Jersey	5	Alum.	On-Stream
Piscataway, Maryland	5	Lime	Const.
Colorado Springs, Colo.	2	Lime	Const.
Santee, California	2	Iron & Alum.	On-Stream

*R & D Studies

Taken from Stephan (1971) (6)

Lime treatment has now become the nucleus of many physical-chemical treatment plants. Not only does lime effectively remove phosphorus, but most investigators report significant reduction in BOD, COD, TOC, suspended solids, and turbidity. Effluents obtained by Buzzell et al (10) after liming to pH 11.0 to 11.5 were of such high quality (80% - 90% total phosphorus removal, 50% - 70% BOD reduction, 25% nitrogen removal, and an important reduction in coliforms) such that subsequent treatment after lime addition and clarification was not necessary. It has also been indicated that physical-chemical treatment has a number of advantages over conventional primary and secondary treatment, such as reduced land requirements, greater flexibility in design and operation, greater opportunities for automation, reduced sensitivity to diurnal flow and loading, and an immunity to upsets by biologically toxic components.

Figures 1 and 2 taken from Stephan (6) outline the most popular physical-chemical treatment system and typical results observed at various stages. The Blue Plains pilot plant has been studied by O'Farrell et al (2) and is described more fully in the extensive literature survey (Appendix C). As revealed in Figure 2, additional filtration, ion exchange and carbon adsorption slightly improved the effluent quality except for nitrogen removal in which case there was a marked reduction. This added protection would be required to meet effluent regulations in some areas of Canada.

The work of Culp et al (7) at Lake Tahoe has shown quite conclusively that ammonia can be readily air stripped out of the wastewater when limed to pH 11.5. (This is also the pH used by O'Farrell et al (8) at Blue Plains.) It should be remembered that the Lake Tahoe wastewater treatment system includes biological treatment, amongst other things, and consequently is far more complex than the Blue Plains system.

Because of conditions peculiar to Canada (small communities, cold climates, limited funds) physical-chemical treatment should gain popularity in this country as well. The first step in this direction was initiated by the Ontario Government as reported by Black et al (9). However, this system still incorporates a biological unit which elevates its cost, complexity, and real estate requirements.

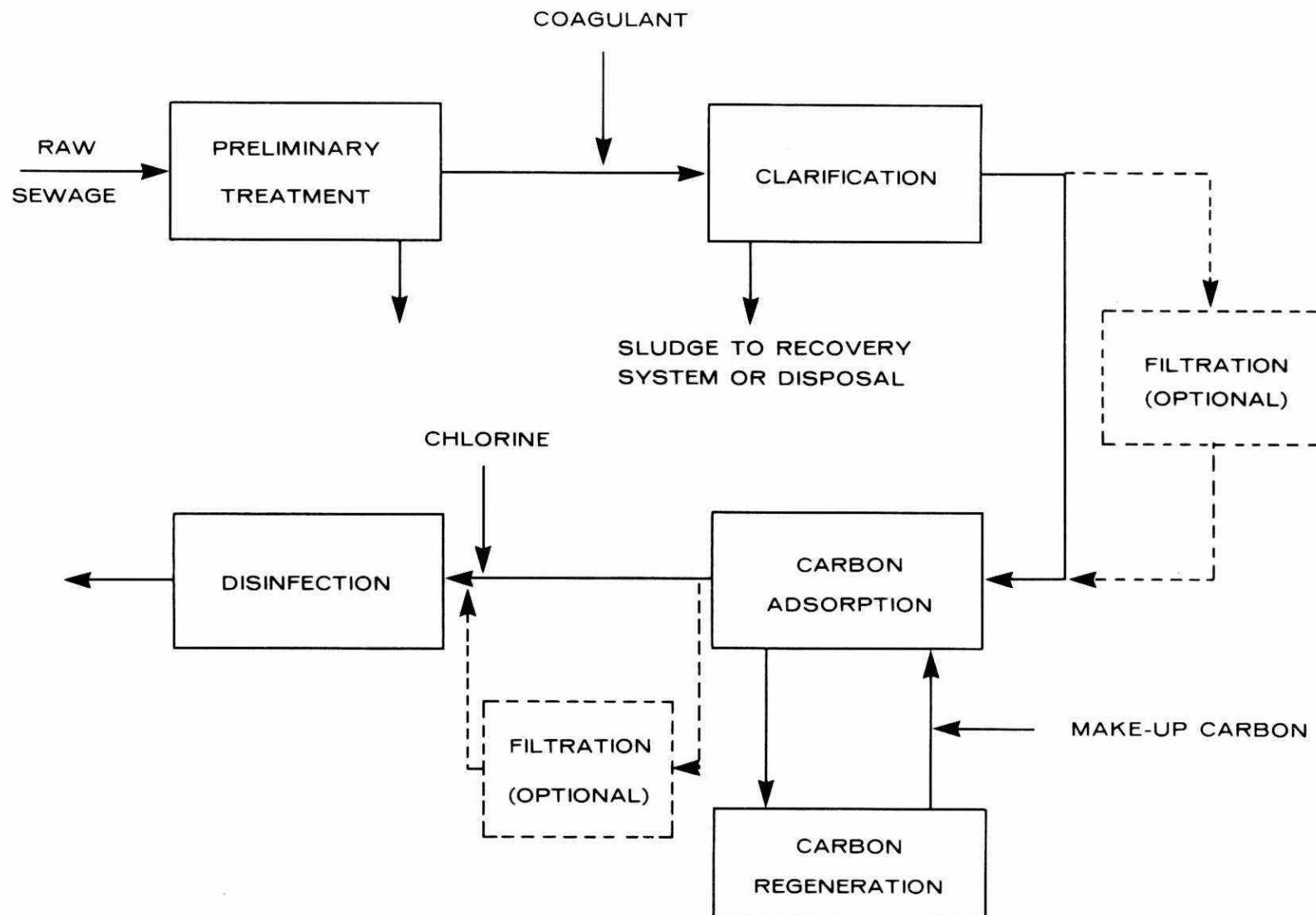


Figure 1 Flow Diagram of a Physical-Chemical Treatment System

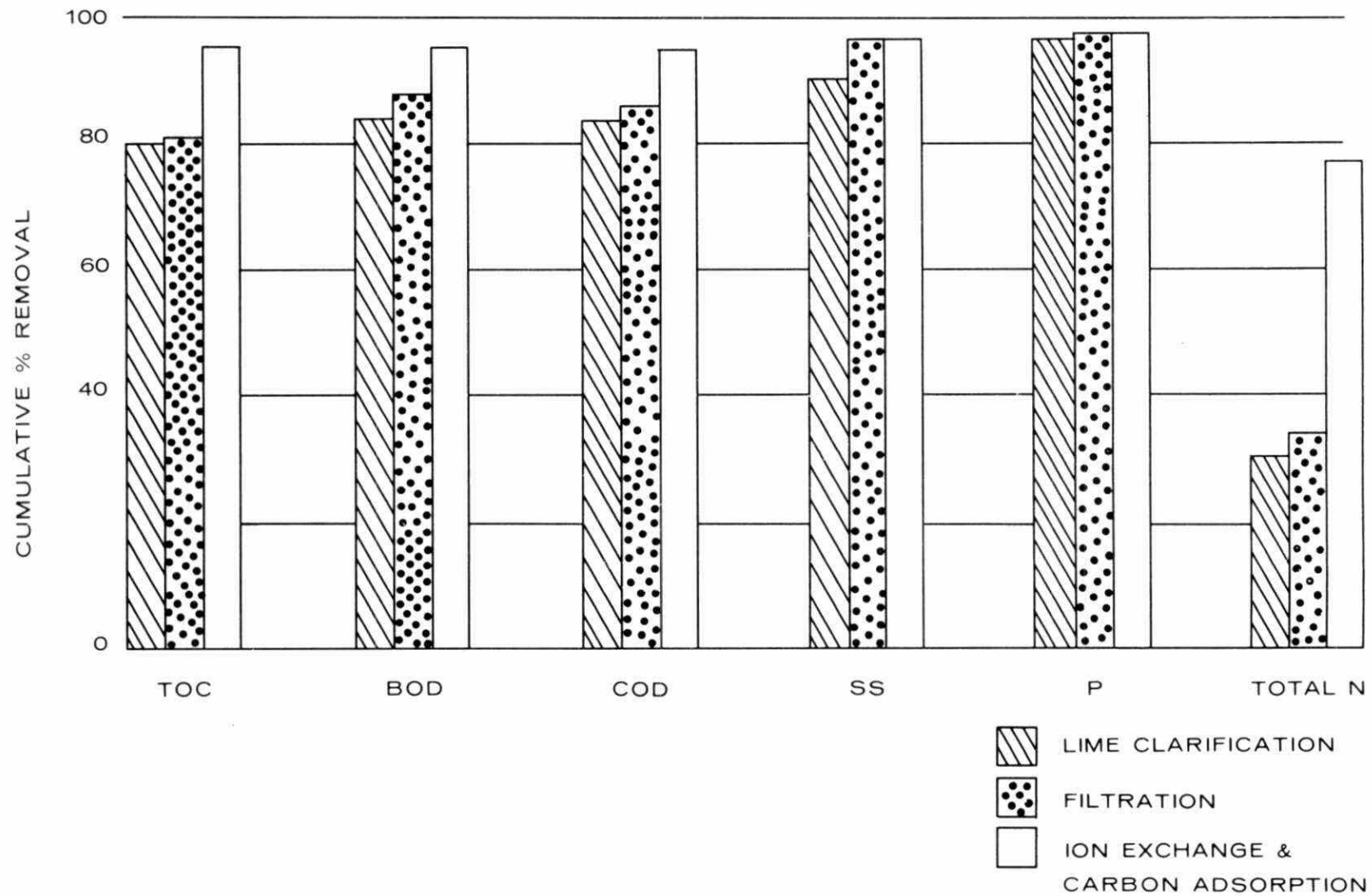


Figure 2 Removal Efficiencies Physical Chemical Treatment Blue Plains Pilot Plant

1.3 Conclusions

Based on the results of the present investigation, the following conclusions have been drawn:

- (1) The addition of lime to pH 9.0 did not consistently remove 80% phosphorus, as reported by some authors. The minimum pH required to achieve good (approximately 1 mg/l) phosphorus removal appeared to be 9.5 - 10.0 and excellent (less than 1 mg/l) phosphate reduction was obtained at pH 11.0 - 11.5.
- (2) The addition of lime to a higher pH such as 11.0 - 11.5 produced an effluent with most of its contaminants removed, e.g.
 - a) COD removals as high as 80% were observed.
 - b) Most of the suspended solids were removed, and, if properly carbonated, levels of less than 15 mg/l were obtained. The effluent turbidity often fell below 1.0 Jackson Turbidity Units.
 - c) BOD reductions were of approximately equal magnitude to those observed for COD.
 - d) All coliform bacteria were destroyed at a pH of 11.5 during a contact period of one hour. Zero coliform discharge from a conventional treatment plant would require massive chlorination.
- (3) Phosphate reduction did not appear to be improved by magnesium addition, regardless of the magnesium content of the water.
- (4) Magnesium additions enhanced the reduction of most contaminants when the initial magnesium content was less than 10 mg/l.
- (5) Iron salts aided in turbidity reduction in the carbonation step.
- (6) The amount of calcium carbonate precipitated during carbonation was variable, depending on the rate of carbonation, the pH to which the effluent was carbonated, and the alkalinity of the effluent prior to carbonation.
- (7) Sludge recycle aided in the reduction of some contaminants but often increased the turbidity. Sludge recycle also appeared to decrease the amount of stirring time required to obtain maximum solids removal.

- (8) Optimum flash mix times and speeds during jar testing appeared somewhat variable. This was tentatively attributed to the amount of magnesium in the sludge.
- (9) Preliminary studies indicated that primary sludge recalcination is feasible.
- (10) Lime treatment should produce an effluent almost equivalent to conventional secondary treatment, unaffected by upsets, surges, or temperature. The cost should be less than primary-secondary treatment, and substantially less than primary-secondary-tertiary systems.

There presently exists a number of wastewater treatment systems, some of which are unsatisfactory for the removal of phosphorus (11). Table 2 clearly indicates that lime treatment appears to be an efficient method for phosphorus removal. Furthermore, the work of O'Farrell et al (2) in Washington (Figure 2) revealed that lime alone was not only excellent for phosphorus removal, but also produced a remarkably good effluent.

The literature survey condensed in Table 2 indicates that lime treatment alone removed from 50% to 80% of the BOD_5 . However, it is realized, and has been stated by the Ontario Water Resources Commission (9) that nitrogen and carbon removal requirements will be dictated by specific receiving water conditions and BOD criteria should be such as to not cause any oxygen deficiency in the receiving water. In the case of many rural Canadian Towns, because of the volume of receiving water available, it would seem unlikely that the remaining 20% to 50% BOD would cause any oxygen deficiency. If a deficiency occurs, then the lime treatment could be followed by treating with activated carbon or biological oxidation. However, of prime importance in the treatment of wastewaters is the sanitary aspect of producing an effluent free of disease causing virus, bacteria, protozoan and other parasites. With regard to eutrophication, phosphorus has been repeatedly demonstrated as the growth limiting nutrient, and should be removed to as low a level as possible.

A number of investigations indicated that high pH lime treatment alone produced an effluent of acceptable sanitary quality which contained only traces of phosphorus. Black and coworkers (20) had demonstrated that the treatment of potable water with lime can be enhanced by the addition of magnesium. It was thought worthwhile to pursue similar investigations on the effect of magnesium in the lime treatment of wastewaters.

The proposed lime system shown in Figure 3 consisted of a degritting chamber prior to a rapid mix chamber where the calcium oxide or calcium hydroxide is added. Immediately after adjusting the pH to 11 or 11.5 depending on the resulting quality of the effluent, magnesium as magnesium chloride or magnesium carbonate is added to the water. The resulting sludge is removed in an appropriately designed clarifier,

TABLE 2

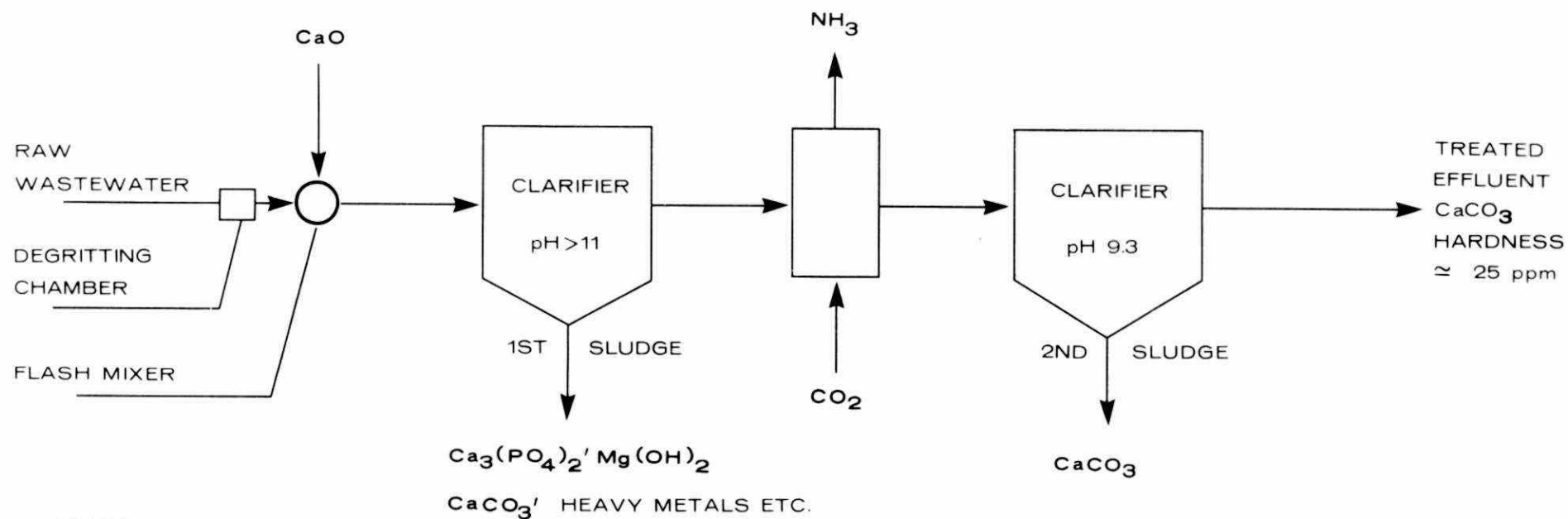
Reported Wastewater Improvement Using Lime Treatment Alone or
in Combination with Either Biological or Chemical Treatment.

System	pH	Phosphorus in-out	BOD in-out	COD in-out	Nitrogen in-out	SS in-out	JTU in-out	Ref. No.
Lime Treatment	9.5+5 mg/l FeCl ₃	14 - 0.4 (97)	220-36 (84)	692-95 (85)	76-34 (55)	371-5 (99)	-	9
Alone	9.4	14 -1.2 (91)	212-40 (81)	586-98 (83)	71-33 (54)	342-8 (98)	-	9
	9.5	9.2-0.3 (97)	78-39 (50)	187-84 (55)	-	109-30 (73)	54-11	12
	9.4	38 -7.1 (80)	-	670-295 (60)	-	312-45 (90)	-	13
	10.8			- (75)		- (91)		14
	11.0	28.5-5.5 (81)	186-54 (71)	355-200 (55)				15
	11.0	3.7-0.37 (91)	100-44 (56)		19-15 (23)			10
	11.0	11.5-1.99 (84)	237-69 (71)		71-54 (24)	(97)		10
	11.4	26 -1.8 (93)	(71)					16
	11.5	9.0- .27 (97)	129-24 (81)	(82)	(32)	48-5.8 (88)		2
	11.5	(96)		100-20 (80)		?-10	?-2	17
Lime Treatment followed by bio- logical system.	9.4	10.7-0.9 (92)	139-5 (96)	408-26 (94)	33-1.2 (96)	221-5 (98)	-	9
	9.4	38 -1.3 (95)		670-70 (90)		312-20 (94)		13
Lime Treatment followed by carbon columns	9.5	9.2-0.3 (89)	76-10 (87)	192-27 (86)	-	109-1 (99)	54-1 (98)	12
Conventional primary and secondary system with lime as tertiary treatment.	11.0	25 -5.2 (79)	(94)					18
	11.0	20 -0.4 (98)	-					18

All values are in mg/l except turbidity and pH

() Data in parenthesis is % reduction.

TWO STAGE PRECIPITATION SYSTEM



12

ONE STAGE PRECIPITATION SYSTEM

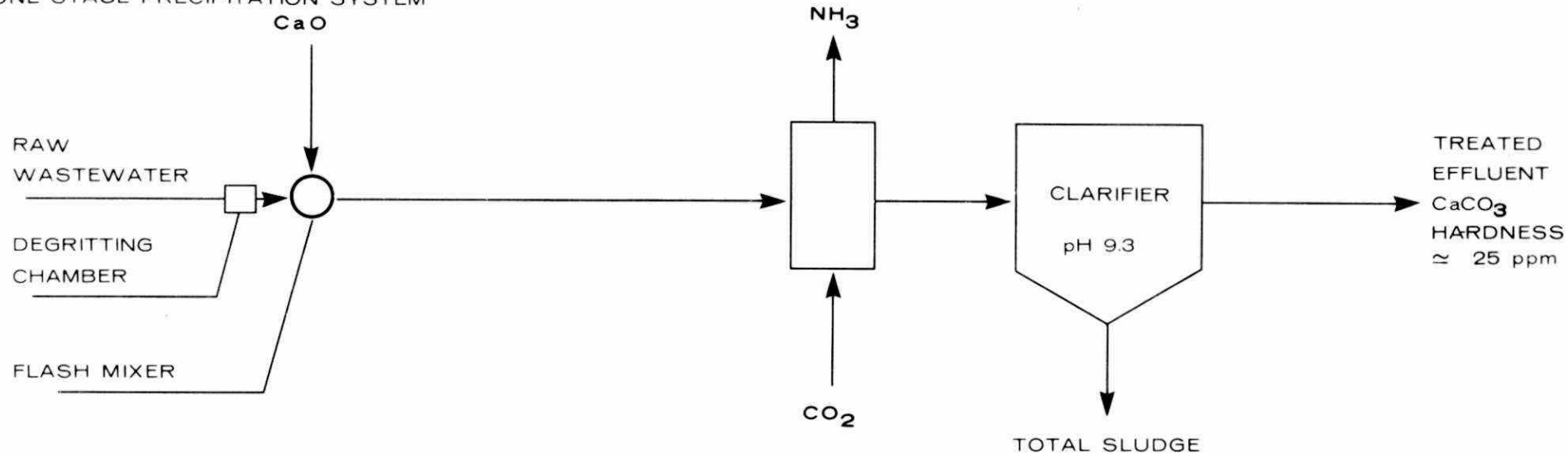


Figure 3 Proposed Lime Treatment Systems

presumably an upflow type. If ammonia removal is also desired, this could be achieved by air stripping followed by carbonation to pH 9. The Turbulent Contact Absorber, which has proven highly efficient in mass transfer when contacting large volumes of liquids or gases, could be used for this purpose.

Carbonation to a pH of approximately 9.3 (lowest solubility of calcium) would ensure an environmentally acceptable effluent. The sludge from this process would also be removed by a clarifier.

As a final step, if desired, the BOD could be reduced by ozonation. Alternatively, the effluent could be passed through activated carbon.

The odour-free and pathogen-free lime treated sludges could be easily disposed of on the surrounding agricultural land, thus enriching the soil with organics, phosphorus, calcium, and other valuable trace elements. The usual absence of industrial activity in most small communities would eliminate any heavy metal problem.

Larger cities would presumably consider calcination of the lime sludges. In such a system, the kiln would incinerate the organics and produce calcium oxide for reuse in the process. In hard water areas, there would be a net production of lime which would have a resale value. The carbon dioxide produced in incineration and calcination could be used in the carbonation phase. If magnesium was found necessary in the optimal functioning of the system, it could be recovered from the primary sludge if financially viable.

The proposed system shown in Figure 3 is particularly well suited to Canadian climate since it is temperature independent except for ammonia stripping. Under these conditions, if ammonium removal was desired, ion exchange columns such as clinopillalite could be used.

In order to evaluate the feasibility of such a treatment system a research program was funded under the Canada-Ontario Agreement on the Lower Great Lakes. The jar testing technique was employed to assess the effect of adding lime to various pH levels and also the effect of

- optimal magnesium ion concentration,
- optimal iron salt concentration,
- polyelectrolyte additions,
- initial bicarbonate concentration, and
- residence time,

on the reduction of

phosphorus,
microorganisms,
trace heavy metals,
COD, TOC, BOD₅,
nitrogen, ammonia,
colour, turbidity, and
odour.

It was also considered valuable to examine the sludge in
terms of:

settling rate,
settled volume,
dewatering characteristics,
ash analysis for phosphate, heavy metals, etc.,
bacterial population density including coliforms,
and calcination to regenerate lime.

3 EXPERIMENTAL

3.1 Remarks

The results reported in the present study were obtained using wastewaters from four different municipalities. The properties of these wastewaters are shown in Table 3.

All analytical procedures were carried out according to the methods suggested by the 13th edition of the "Standard Methods for the Examination of Water and Wastewater".

3.2 Pincourt Raw Wastewater Study

Since there were no daily records at Pincourt on suspended and dissolved solids, sludge volume, COD, BOD, and phosphorus content, it became necessary to establish these levels at various times during the week. Repeated sampling indicated that the raw wastewater was very weak presumably since the sewage becomes diluted with surface waters.

Because no other conveniently located municipality with secondary treatment had a stronger raw wastewater, it was decided to carry out preliminary experimentation until a more appropriate source could be found, or until the surface waters froze.

3.3 Effect of pH on a Weak Raw Wastewater (Low Organic Strength)

The first experiment was designed to determine the effect of lime addition to three different levels (pH 9, 10, and 11) with and without magnesium additions. The results are presented in Table 4. Unfortunately, at the time of sampling, the BOD_5 was only 13 mg/l. The alkalinity of the influent was 240 mg/l calculated as $CaCO_3$, while the calcium and magnesium concentrations were found to be 86 and 29 mg/l, respectively.

It is interesting to note that the magnesium level began to decrease after pH 9.0 and was quite low by 11.5. (See Figure 4.)

The results indicated quite clearly that lime treatment at most of the concentrations examined was superior in all measured parameters to biological treatment observed at this plant. However, the general validity of such a conclusion had to await experimentation with a stronger effluent. The role of magnesium was not too clear, for no definite trend could be discerned from these results. Of interest is the

TABLE 3

Some Properties of Wastewater Used in Lime Treatment Studies

Municipality	Present Treatment System	Alkalinity mg/l as CaCO_3	Magnesium mg/l	Ca(OH)_2 req'd for pH 11.5 mg/l*
Pincourt, Que.	Primary & Secondary	240	29	550
Beaconsfield, Que.	Primary	310	36	580
Ottawa, Ont.	Primary	140	11.3	330
Red Rock, Ont.	None	65	4.2	211

*Based on percent lime activity \geq 98%. Average lime dose values: can expect deviation according to "strength" of the wastewater.

TABLE 4 Effect of Adding Lime in Pincourt Wastewater to Various pH Levels With and Without the Addition of Magnesium

	Wt. of* Ca(OH) ₂ (mg/l)	pH	mg/l Mg ⁺⁺ added as MgCl ₂	Sludge Vol.** (ml)	mg/l				Total Coliforms per 100 ml	Fecal Coliforms per 100 ml	Ca ⁺⁺ mg/l remaining at end of treatment	Mg ⁺⁺ mg/l remaining at end of treatment
					BOD ₅	COD	Suspended Solids (SS)	Ortho PO ₄ as P				
Raw Wastewater	0	7.3	0	0.1	13	47	10	2.4	1.6 x 10 ⁶	7.0 x 10 ⁵	86	29
Biologically Treated Effluent***	0	7.3	0	0.1	11	42	3	2.2	3.0 x 10 ²	2.0 x 10 ²	79	26
Flask 1	90	9.0	0	0.6	12	37	12	1.9	7.0 x 10 ⁵	7.0 x 10 ⁵	106	29
2	90	9.0	21	0.5	13	37	18	1.4	N.S.	N.S.	95	33
3	350	10.0	0	10.0	9	19	10	0.1	0	0	59	18
4	350	10.2	21	16.0	9	19	12	<0.02	N.S.	N.S.	57	13
5	500	11.1	0	24.0	9	19	8	<0.02	0	0	108	1.3
6	500	11.1	21	24.0	9	19	10	<0.02	0	0	365	lost

* Test conditions: In this and all subsequent jar tests, rapid mixing was at 100 rpm for 10 min,
slow stirring at 30 rpm for 5 min.

** Sludge Volume is defined as the volume (ml) of sludge present in an Imhoff cone after 1 hour.

*** Conventional Activated Sludge treatment systems.

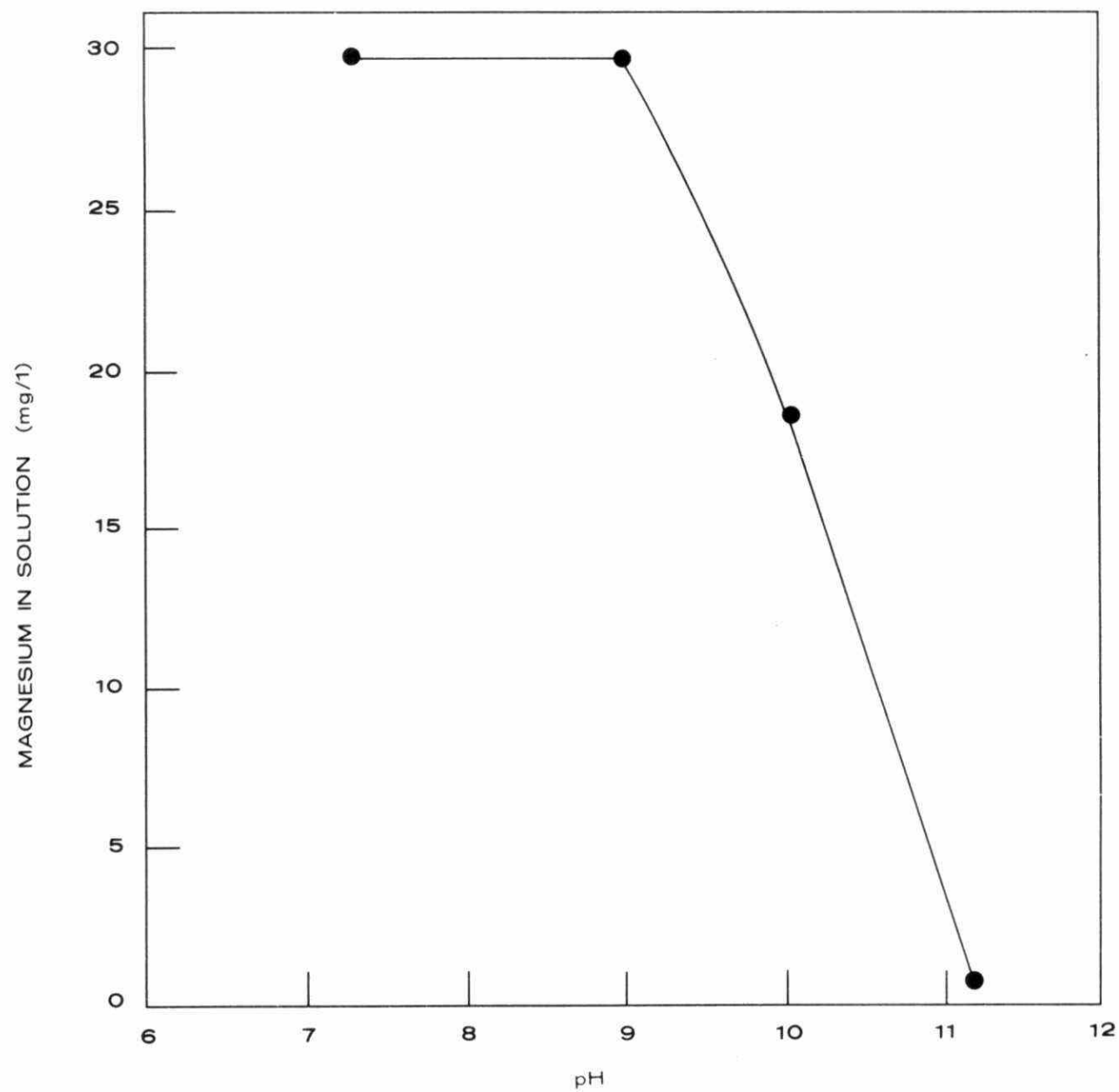


Figure 4 Effect of pH on Magnesium Level in Supernatant

marked decrease in total and fecal coliforms found between effluents treated with lime to pH 9 and 10 respectively.

3.4 The Effect of Magnesium on a Weak Effluent

To elucidate the effect of magnesium in lime treatments, six samples were adjusted to pH 11.5 by the addition of 500 mg/l $\text{Ca}(\text{OH})_2$. Magnesium (as MgCl_2) was added in amounts varying between zero and 100 mg/l as shown in Table 5. After the sludge settled, the supernatant was collected and the pH readjusted to 9.5 by the addition of sodium bicarbonate. This method of neutralization, as compared to saturation with carbon dioxide, would increase the dissolved solids.

No beneficial effect was observed from the addition of 100 mg/l magnesium ion except for an apparent decrease in dissolved solids. This apparent lack of enhancement of lime treatment with the addition of magnesium may have been due to the high background concentration of Mg^{++} in the wastewater and the weakness of the wastewater.

The decrease in orthophosphate from 0.01 to zero mg/l phosphorus is not significant (Table 5). The 86% reduction in BOD_5 (50 to 7 ppm) is encouraging but this determination should be repeated on normal strength effluent to be significant. The microbial quality of the effluent was exceptionally good since all coliforms were destroyed. The total plate count on the supernatant was lower than that found in many lakes and rivers approved for bathing. The sludges were also examined for their microbial content to determine if such material could be safely land disposed. They were found to contain relatively few bacteria.

The data in Table 5 was obtained from samples collected January 10, 1973 in the midst of a "cold snap" when any surface waters would have frozen. The weakness of the effluent collected under these climatic conditions can only be taken to indicate that there is sub-surface infiltration of water into the sewer system, so a different site had to be chosen to obtain stronger effluent.

3.5 Beaconsfield Wastewater Study

After sampling at various localities for stronger effluent, that at Beaconsfield, Que., was found to be the strongest. It was decided

TABLE 5

The Effect of High pH and Various Mg^{++} Levels on Pincourt Effluent Characteristics (5)

	pH	mg/l Mg^{++} added as $MgCl_2$ (1)	Sludge Vol. (ml) (2)	Weight of sludge (g)	Sludge Percent Solids	mg/l				SUPERNATANT (4)		S L U D G E	
						BOD ₅	COD	Susp. solids	Ortho PO_4 as P	Total plate count/ 100 ml	Total Coli- forms/ 100 ml	Total plate count per 100 ml pH NOT adjusted	Total plate count per 100 ml pH adjusted to 7
Raw Wastewater	7.4	-	1.5	0.012	0.78	50	50	14	1.3	1×10^7	3×10^5	-	-
Flask 1	11.4	0	29	0.595	2.05	7 (86)	14 (72)	24	0.01 (99)	9×10^2	0	11.7×10^3	8.4×10^3
2	11.4	5	29	0.603	2.08	7 (86)	14 (72)	23	0.01 (99)	5×10^2	0	11.8×10^3	9.4×10^3
3	11.5	10	28	0.593	2.12	7 (86)	14 (72)	28	<0.01 (99)	17×10^2	0	12.9×10^3	8.3×10^3
4	11.4	20	32	0.595	1.86	7 (86)	23 (54)	15	<0.01 (99)	0 (?)	0	8.6×10^3	11.8×10^3
5	11.5	40	32	0.640	2.00	7 (86)	18 (64)	21	0	1×10^2	0	10.5×10^3	10.4×10^3
6	11.4	100	36	0.673	1.87	7 (86)	14 (72)	21	0	1×10^2	0	10.3×10^3	9.3×10^3

(1) Background Mg^{++} is 29 mg/l. 550 mg/l $Ca(OH)_2$ was required to adjust non magnesium supplemented wastewater to pH 11.5

(2) Ml of sludge in Imhoff after one hour.

(3) Determined at pH 9.5; neutralized with $NaHCO_3$, resulting in an increase of dissolved solids.

(4) pH adjusted to 9.4; counts on supernatant after one hour settling.

(5) Lime treatment of raw wastewater followed by recarbonation to pH 9.5 with sodium bicarbonate.

() Data in parentheses are percent reduction.

that future studies should be undertaken with this effluent even though the municipality had only primary treatment facilities.

3.6 Effect of Magnesium on a Stronger Effluent

A repetition of the work carried out previously was undertaken with the stronger Beaconsfield effluent. The results of these tests are presented in Table 6.

As had been previously observed, no magnesium effect could be detected even in a stronger effluent. The BOD_5 was reduced by 80% (145 to 30 mg/l) and the COD was reduced by approximately 60% (160 to 60 mg/l).

The residual phosphorus level in this trial was greater than previously observed. The slightly greater concentration of phosphorus with 100 mg/l Mg^{++} is within experimental error and may have been related to the elevated suspended solids. Nevertheless these levels of phosphorus residues exceed the requirements of even the most stringent regulations.

The supernatant was devoid of all coliforms and showed a 10^4 decrease in total bacteria. In an attempt to determine if there was a decrease in viable bacteria with increased residence time in the lime sludge, the bacteria were enumerated after one and 24 hours. There was no significant change in population after one or 24 hours.

3.7 Variability in Strength of Beaconsfield Wastewater

The strength of Beaconsfield wastewater was subject to large variation from one day to another. The inconvenience of such variability in experimental material for jar testing (85% and 70% COD change between January 22 and 24 at 10:30 AM) needs no elaboration. However, such fluctuations were extremes and most samples were more closely clustered.

3.8 Supplemental Phosphorus Addition to Combination of Lime and Magnesium Treatment

Since no marked improvement was evidenced by the addition of magnesium to an effluent at pH 11.4 (Section 3.6), it was speculated that perhaps the low phosphorus level (3 mg/l) caused the formation of such a small amount of calcium hydroxyapatite that the indigenous magnesium provided sufficient coagulation to remove the apatite.

TABLE 6

The Effect of High pH and Various Mg^{++} Levels on Beaconfield Effluent (5)

	pH	mg/l Mg ⁺⁺ added as MgCl ₂ (1)	Sludge Volume (ml) (2)	Sludge Weight (g)	Sludge % Solids	mg/l						Total Plate count per 100ml	Total Coli- form/ 100ml	Total plate count/g sludge (4)		Total Alka- linity mg/l as CaCO ₃
						BOD ₅ (3)	COD	S.S.	Ortho PO ₄ as P	Poly PO ₄ as P	Total PO ₄ as P			after 1 hr	after 24 hr	
Influent	7.5	-	5	0.037	0.74	145	160	65	2.1	0.9	3.0	20x10 ⁶	23x10 ⁵	1.7x10 ⁹	1.7x10 ⁹	310
Flask 1	11.4	0	32	0.835	2.61	30 (79)	70 (56)	35	0.04	0.04	0.08 (97)	32x10 ²	0	>10 ⁴	8.5x10 ⁴	140
2	11.5	5	32	0.869	2.72	30 (79)	65 (59)	35	0.03	0.05	0.08 (97)	60x10 ¹	0	>10 ⁴	8.4x10 ⁴	140
3	11.4	10	34	0.880	2.59	30 (79)	45 (71)	26	0.015	0.07	0.08 (97)	13x10 ²	0	>10 ⁴	8.4x10 ⁴	140
4	11.4	20	35	0.833	2.38	30 (79)	60 (62)	60	0.05	0.02	0.07 (98)	46x10 ²	0	>10 ⁴	8.8x10 ⁴	140
5	11.4	40	33	0.888	2.69	30 (79)	60 (62)	75	0.04	0.04	0.07 (98)	27x10 ²	0	>10 ⁴	8.3x10 ⁴	140
6	11.4	100	41	0.859	2.10	30 (79)	50 (69)	115	0.04	0.06	0.10 (96)	13x10 ²	0	>10 ⁴	8.4x10 ⁴	140

(1) Background Mg^{++} is 35.6 mg/l. 580 mg/l $Ca(OH)_2$ required to adjust non-magnesium supplemented wastewater to pH 11.5.

(2) Ml of sludge in Imhoff after one hour.

(3) Samples readjusted to pH 7. Other analysis (COD, solids, phosphorus, and bacterial counts on supernatant carried out at pH 8.7 by CO_2 saturation.

(4) Expressed on a g dry weight basis. Parallel samples dried overnight at 105°C.

(5) Lime treatment of raw wastewater followed by recarbonation to pH 8.7 by CO_2 saturation.

* = Suspended solids

** = Dissolved solids

To verify this, three levels of phosphate (0, 5, 10 mg/l as P) were added to wastewater containing 10.8 mg/l phosphorus (as P). Twenty mg/l of Mg^{++} as magnesium chloride were added to one of the duplicates to ascertain if there was any difference between remaining phosphorus levels and the presence and absence of magnesium. As shown in Table 7, irrespective of the pretreatment, COD and phosphorus revealed no improved removal over the non-treated systems. The magnesium supplementation did aid in turbidity reduction and this was the first evidence that the presence of magnesium improved the quality of lime treated effluents.

3.9 Low pH Treatment of Wastewater with and without Magnesium and with and without Sludge Recycle

Since a number of publications indicated that pH 10 was sufficient for phosphorus removal, (see Literature Review, Appendix C, and Table 2) it was decided to investigate the effect of magnesium as well as sludge recycle at this low pH.

As shown in Table 8, treatment to pH 10.0 resulted in approximately 60% reduction in suspended solids, 64% reduction in phosphorus, and 60% reduction in COD whether magnesium was added or not. When 10% sludge was recycled into parallel samples pH control was more difficult in the jar tests. Suspended solids revealed considerable variation with no apparent trend. Phosphorus and COD removals tended to be slightly less.

From these results, it was tentatively postulated that:

- 1) a pH of 10.0 was less efficient for phosphorus removal than pH 11.5 (see Table 7),
- 2) there was no significant difference in percent reduction of COD between pH 10 and 11.5,
- 3) magnesium had no obvious beneficial effect at pH 10,
- 4) sludge recycle did not appear to have any effect at pH 10.0,
- 5) iron (50 mg/l Fe^{++} as $FeCl_3$) appeared to lower the effluent quality at pH 10.

3.10 Effluent Quality as a Function of pH and Recycle

To further elucidate the effect of pH on the quality of lime treated wastewaters, duplicate samples of Beaconsfield effluent were

TABLE 7

Phosphorus Removal at pH 11.5 in Wastewaters
Supplemented with Phosphate with and without
Magnesium Addition.

Sample	Chemicals added prior to pH adjustment		Analysis of Supernatant after carbonation (pH 8.3) and settling for one hour.		
	mg/l PO ₄ addition as P	mg/l Mg ⁺⁺ addition	C.O.D. mg/l	Turbidity J.T.U.	Total Phosphorus mg/l
Control	0	0	595	118	10.8
Flask 1	0	0	235 (61)	0.36	0.48 (95.6)
2	5	0	235 (61)	0.52	0.112 (99.0)
3	10	0	235 (61)	0.40	0.092 (99.2)
4	0	20	225 (62)	0.26	0.072 (99.3)
5	5	20	235 (61)	0.28	0.056 (99.5)
6	10	20	230 (61)	0.27	0.056 (99.5)

Figures in parenthesis are percent reductions
 Phosphorus added as Na₂HPO₄

TABLE 8

Low pH Treatment of Beaconsfield Raw Wastewater With and Without Magnesium
With and Without Iron Salts, With and Without Sludge Recycle (4)

Flask No.	pH	Ca(OH) ₂ mg/l	Mg ⁺⁺ mg/l (1)	Recycle 25 ml sludge from (2)	Fe ⁺⁺ mg/l (3)	Final pH after carbon- ation	S.S. mg/l	Total PO ₄ mg/l as P	COD mg/l
Control	7	-	-	-	-	-	50	7.3	225
1	10	250	0	none	-	8	20 (60)	2.6 (64)	90 (60)
2	10	250	10	none	-	8	25 (50)	2.6 (64)	90 (60)
3	10	250	50	none	-	8	15 (70)	2.6 (64)	90 (60)
4	10	250	100	none	-	8	20 (60)	3.6 (50)	110 (51)
5	10.6	250	0	Flask 1	-	7	10 (80)	2.8 (62)	65 (71)
6	11.0	250	0	Flask 2	-	7.4	25 (50)	6.6 (9.5)	100 (56)
7	10.7	250	0	Flask 3	50	7.0	40 (20)	3.6 (50)	95 (58)
8	10.1	250	0	Flask 4	50	10.1	10 (80)		60 (73)

(1) as MgCl₂

(2) Sludge for recycle obtained after one hour settling in an Imhoff cone.

(3) as FeCl₃

(4) Lime treatment of raw wastewater followed by recarbonation.

adjusted to pH levels between 10 and 11.5 in increments of 0.5 pH units. The first series of the duplicate samples received no sludge, while the second series received 10% sludge from its corresponding duplicate.

In the non-sludge recycled series, the level of suspended solids and phosphorus remaining in the supernatant decreased with increasing pH (Table 9). The reduction of bacteria count resulting from increased pH is also noteworthy. Reduced COD levels, though not consistent, were also generally observable with increased pH. From these data, it appears that the only advantage of increasing the pH from 11 to 11.5 was the complete destruction of coliforms. The decrease in total bacteria counts from 9.3×10^5 to 2.3×10^3 per 100 ml was a substantial 90% decrease in population but the surviving 10^3 bacteria/100 ml still represent heavy contamination.

In the sludge recycle series, there was a definite reduction in suspended solids at all pH levels, except at 11.5 where the high value may have arisen from contamination. Other parameters, except for increased sludge weight and volume, appeared unaltered whether sludge was recycled or not. The trend was increased removal of contaminants with increased pH, but this was less evident than in the system without sludge recycle.

Figure 5 illustrates sludge production versus phosphorus removal and suspended solids reduction at various pH levels. It would be necessary to determine at each location whether the increased phosphorus reduction and coliform elimination justifies handling the increased sludge weight, especially between pH 11.0 and 11.5.

3.11 pH and Bacterial Numbers

One of the advantages of lime treatment is the possible destruction of disease producing organisms. Throughout this project, microbial analyses were performed to estimate the effect of lime addition on bacterial count. These results indicated that a pH of 11.5 was required for complete elimination of total coliforms.

One experiment was designed solely for the evaluation of coliform and total bacteria survival in wastewaters treated with lime to various pH levels. Samples of fresh sewage were pH adjusted, then rapidly mixed

TABLE 9

Beaconsfield Effluent Quality* as a Function of pH and Sludge Recycle

Lime Addition to pH	SETTLEABLE SOLIDS		SOLIDS - SUPERNATANT (mg/l)		PHOSPHATE (mg/l as P)		COD (mg/l)	BACTERIA/100 ml	
	Sludge Volume (ml)	Sludge Weight (g/l)	S.S.	T.S.	Ortho PO ₄ as P	Total PO ₄ as P		Total Bacteria	Total Coliform
Influent	-	-	90	795	5.2	6.2	165	1.4×10^7	9.3×10^5
10.0	9	0.46	32 (65)	672	0.63 (88)	0.56 (91)	50 (70)	2.1×10^6	2.3×10^5
10.5	12	0.46	25 (72)	675	0.26 (95)	0.52 (92)	20 (88)	4.5×10^5	4.3×10^4
11.0	20	0.57	15 (83)	665	0.08 (98)	0.25 (96)	35 (79)	1.0×10^5	2.3×10^3
11.5	38	0.68	16 (82)	656	0.075 (98)	0.18 (97)	25 (85)	5.7×10^4	0
WITH SLUDGE RECYCLE** FROM CORRESPONDING TESTS ABOVE									
10.0	13	0.60	15 (83)		0.54 (90)	0.62 (90)	45 (73)	-	-
10.5	15	0.72	5 (94)		0.08 (98)	0.32 (95)	40 (76)	-	-
11.0	17	0.74	5 (94)		0.05 (99)	0.20 (97)	10 (94)	-	-
11.5	45	0.73	55 (39)		0.46 (88)	0.52 (92)	25 (85)	-	-

() Data in parenthesis represents percent reduction.

* Analysis on effluent carbonated to pH 8.4.

** 10% solids produced in flasks 1, 2, 3, and 4 was added to flasks 5, 6, 7, 8 respectively.

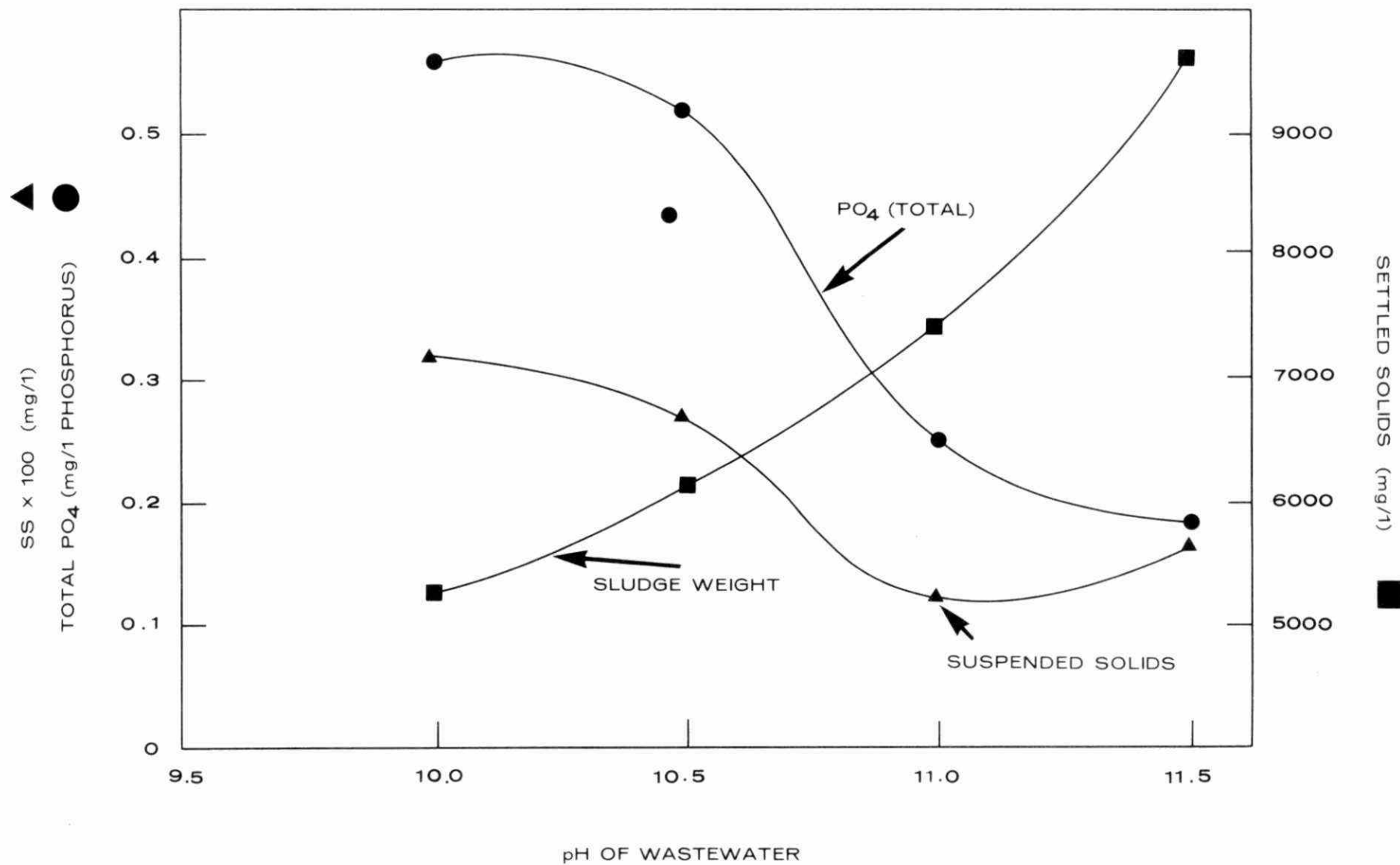


Figure 5 Residual PO_4 in Supernatant and Total Settled Solids as a Function of pH in Beaconsfield Municipal Sewage.

at 100 rpm for 15 minutes and slowly mixed at 30 rpm for five minutes. The supernatant was sampled after a settling period of 40 minutes, thus making the total contact time one hour.

Serial dilutions from 10^0 to 10^7 were prepared in sterile saline, five replicate 10 ml samples being taken for each treatment. The membrane filtration technique was employed for the enumeration of microorganisms. All filters were rinsed with sterile saline (0.75%) after each sample, thus ensuring that the organisms were exposed to the high pH only for the specified time.

The results, which are shown in Figure 6, indicate there was little decrease in populations until pH 10, after which they decreased very rapidly. (It should be noted that the results are expressed in number of bacteria per milliliter.) The last 0.5 pH units between pH 11.0 and 11.5 appear to be quite necessary for the total destruction of coliforms during a one hour contact period. Presumably, within limits, longer contact times would reduce the pH required to eliminate the coliforms. As indicated by the total bacteria count, this type of treatment does not produce a sterile effluent within a one hour contact time. It is believed that there would be little microbial activity in sludge stored at pH 11.5, even though some organisms may survive.

3.12 Iron Salts in Lime Treated Wastewaters

A series of jar tests was undertaken to evaluate the effect of iron in lime (pH 11.5) treated effluents. As shown in Table 10, the iron, dosed at 5 mg/l, was added before and after one hour settling of the sludge.

No difference in suspended solids could be detected, regardless of the treatment. Phosphorus removal was also independent of the system employed, except for one case which was presumably a technical error. Of interest, however, is the reduction in COD and turbidity of all samples treated with iron; the increase from 40% to 60% COD removal is quite significant.

3.13 Effect of Duration of Stirring on Effluent Quality

All previous jar tests were carried out with stirring at 100 rpm for 15 minutes followed by five minutes at 30 rpm. However, it was

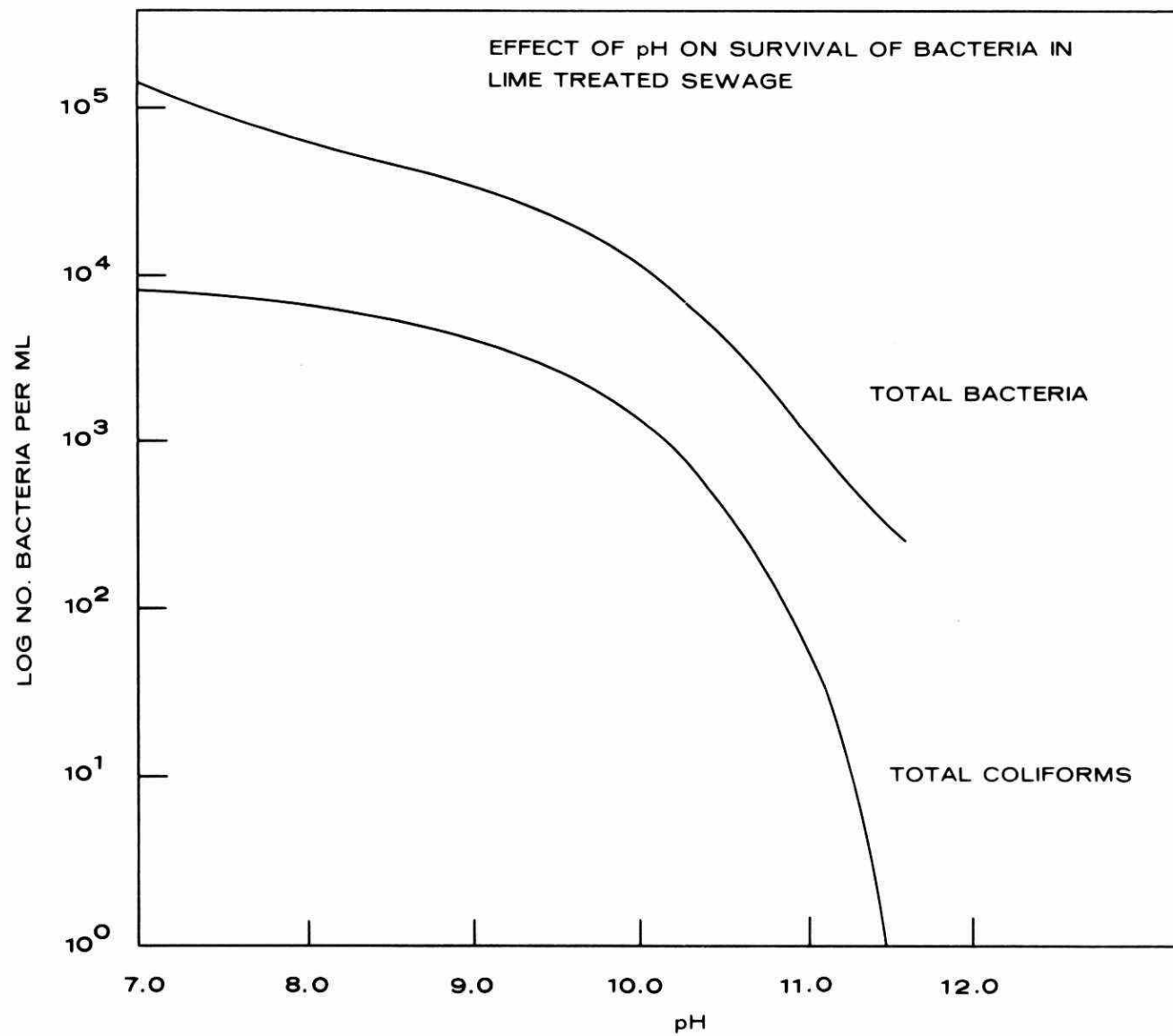


Figure 6 Beaconsfield Municipal Effluent.

TABLE 10

Effect of High pH and Iron Addition at Various
Points on the Quality of Beaconsfield Effluent

Sample Treatment	S.S.	Turbidity J.T.U.	Total PO_4 as P	C.O.D.
Control	100	30	1.15	50
pH 11.5; settled 1 h, carbonated to pH 9.5; settled 1 h	<1 (99)	2.5	0.032 (97)	30 (40)
pH 11.5; carbonated to pH 9.5; settled 1 h	<1 (99)	2.4	0.11 (90)	30 (40)
pH 11.5; 5 mg/l Fe^{+++} ; carbonated to pH 9.5; settled 1 h	<1 (99)	1.6	0.034 (97)	25 (50)
pH 11.5; carbonated to pH 9.5 5 mg/l Fe^{+++} settled 1 h	<1 (99)	0.95	0.034 (97)	25 (50)
pH 11.5; 5 mg/l Fe^{+++} settled 1 h carbonated to pH 9.5; settled 1 h	<1 (99)	1.3	0.043 (96)	20 (60)
pH 11.5; settled 1 h; 5 mg/l Fe^{+++} added to pH 9.5; settled 1 h	<1 (99)	1.25	0.030 (97)	20 (60)

- Data in mg/l except where stated otherwise.

- Data in parenthesis are percent reduction.

recognized that such conditions may not have been ideal. Hence a range of stirring times, from zero to 60 minutes, was evaluated including two samples which were not stirred but merely received one percent and 10% sludge recycle from a sludge also produced under agitation free conditions.

The 95% reduction in suspended solids and 72% - 75% removal in COD (Table 11) in the non-stirred, sludge recycle system was superior to all other treatment results. However, the effluent remained quite turbid in the 10% and 1% sludge recycle system (24 and 6.8 JTU respectively).

Where there was no sludge recycle, suspended solids removal was optimum after 15 minutes stirring and turbidity after five minutes stirring (Figure 7). For phosphorus and COD reduction, stirring time did not seem to make any difference.

To further elucidate the sequence and duration of stir times, an experiment was designed to determine which stir conditions engendered the most rapid sludge formation and produced the least turbid effluent. COD and phosphorus were not determined since the previous experiment (Table 11) had revealed that these two parameters seemed relatively constant regardless of stir time.

The effluent was treated to pH 11.5 prior to being stirred for either a 10 or 15 minute period. As shown in Table 12, these periods were made up of a combination of fast (100 rpm) and slow (30 rpm) stirring speeds.

The results indicated that rapid mixing for a short period followed by slow mixing for a longer period produced the least volume of sludge and the least turbidity. From Table 12, the best mixing conditions, at least for jar testing, appeared to be stirring for one minute at 100 rpm and 14 minutes at 30 rpm followed by a settling period of 30 minutes.

3.14 High pH Treatment on Low Magnesium Waters

Since the Ottawa River near Montreal contains rather high concentrations of magnesium (35.6 mg/l at Beaconsfield and 29 mg/l at Pincourt), it was speculated that supplemental addition of magnesium had no beneficial effect. To circumvent this difficulty, samples were collected at the Greens Creek treatment plant in Ottawa, where the background magnesium was 11.3 mg/l.

TABLE 11 Effect of Stirring Time on the Quality of
Beaconsfield Effluent Adjusted to pH 11.5

Sample Treatment	S.S.	COD	PO ₄ as P	Turbidity J.T.U.
Control	238	270	5.0	34.0
Stirred 60 min	64 (73)	95 (65)	0.17 (97)	3.7
Stirred 15 min	38 (84)	- (96)	0.19 (96)	2.2
Stirred 5 min	50 (79)	95 (65)	0.20 (96)	1.8
Stirred 0 min	110 (53)	85 (69)	0.036 (99)	4.7
10% of sludge from zero stir time sample stirred 0 min	13 (95)	75 (72)	0.070 (98)	24.0
1% of sludge from zero stir time sample stirred 0 min	11 (95)	68 (75)	0.048 (99)	6.8

- All data in mg/l except where stated otherwise.
- Stirring speed 100 rpm.
- Carbonation of sample was performed without removing the first lime sludge.

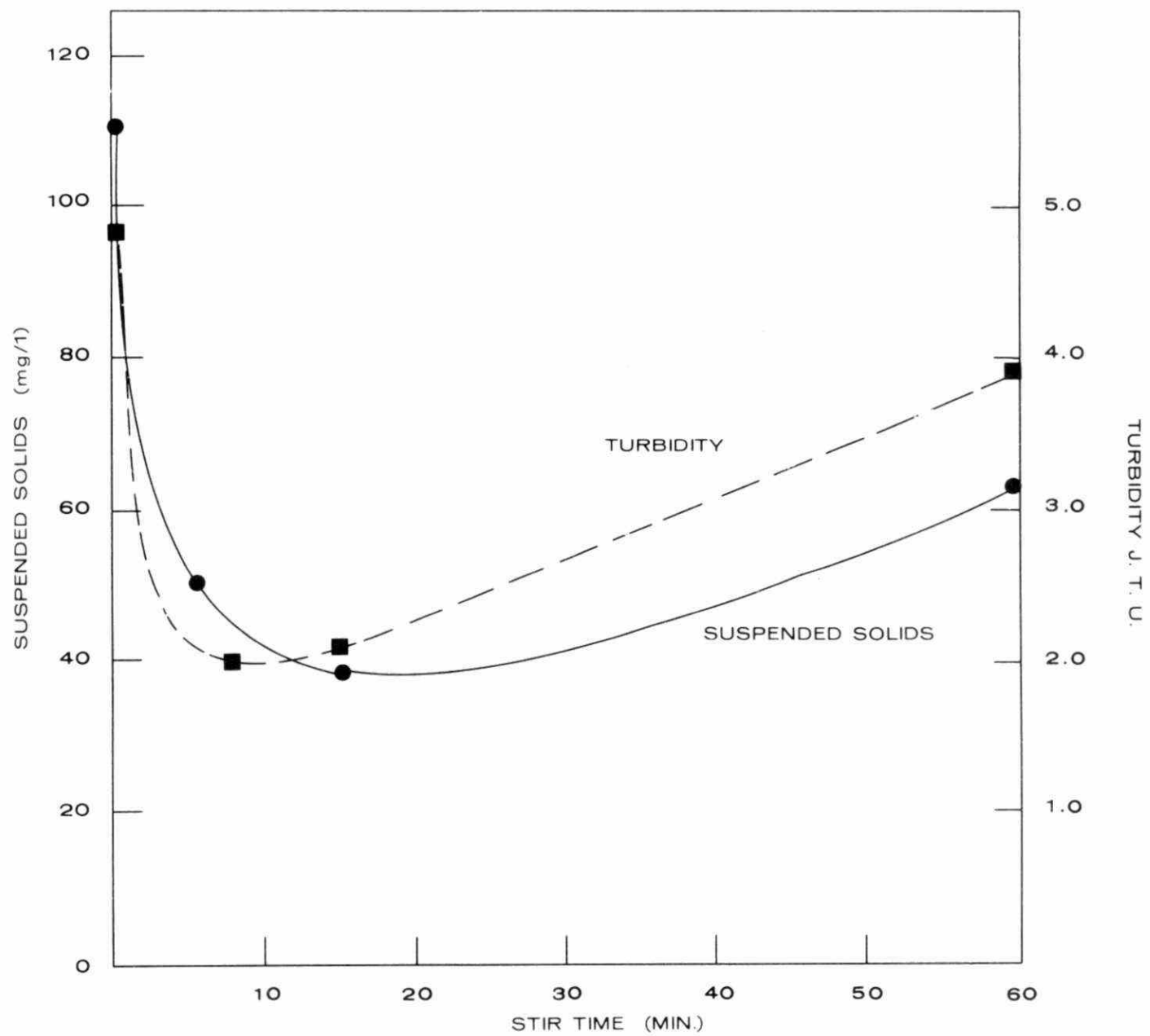


Figure 7 Effect of Stir Time On Suspended Solids and Turbidity.

TABLE 12

BEACONSFIELD MUNICIPAL SEWAGE

Effect of Rapid and Slow Stirring Time on Sludge Volume and Turbidity on Beaconsfield Effluent.

Duration (Minutes) of stir at		Total Stir Time (min)	Vol. (ml) of settled solids in Imhoff conc. after ... min						Turbidity (J.T.U.) after ... min					
100 rpm	30 rpm		5	10	15	30	45	60	5	10	15	30	45	60
1	14	15	15	12	9.5	8.0	7.5	8.5	38	17	10	4.8	4.7	3.9
3	12	15	18	14	12	11	10	11	48	39	22	7.3	7.3	5.3
5	10	15	18	13	11	11.5	10	11	64	67	29	9.1	9.0	6.8
9	6	15	18	14	11.5	11	10	10.5	47	28	18	7.0	5.4	4.4
13	2	15	22	17	14	14.5	13	14	47	24	22	10.0	6.9	7.3
15	0	15	21	16	13	14	12	13	50	22	17	9.0	3.5	3.5
1	9	10	8	10	10	8.5	7.5	7.5	62	N.S.	12	8	3.6	3.0
3	7	10	24	20	17	12	11.5	11.5	47	N.S.	28	14	15.4	6.5
5	5	10	16	15	16	12	10.5	10.5	43	N.S.	29	22	8.7	7.7
7	3	10	21	19	19	14.5	13	14	38	N.S.	24	16	4.8	4.7
9	1	10	25	19	18	12	11	11	35	N.S.	27	13	5.2	5.2
10	0	10	28	20	18	12	11	11	33	N.S.	29	18	6.9	6.9

All tests carried out at pH 11.5 - (550 mg/l Ca(OH)_2) with no carbonation.

Jar tests were carried out on the effluent supplemented with various concentrations of magnesium, ranging from zero to 100 mg/l and adjusted to a pH of 11.5.

The samples were unfortunately quite weak (COD of 86 mg/l) (Table 13), but nevertheless an interesting trend was discernible. Suspended solids removal was quite good with magnesium additives from zero to 40 mg/l. At magnesium additives of 100 mg/l, there was a sudden rise in suspended solids. The magnesium remaining in the supernatant paralleled the suspended solids remaining in the supernatant. This would suggest that suspended solids removal at high pH was dependent upon the degree of magnesium hydroxide remaining in solution.

Turbidity showed a somewhat more complex relationship. There was approximately a 50% reduction in turbidity with the addition of 5 mg/l magnesium when compared with the control to which no magnesium was added. When 20 or 40 mg/l of magnesium were added, the turbidity dropped to 80% of the control. Beyond 40 mg/l magnesium addition, the turbidity began to increase. Optimal turbidity removal also appears to parallel magnesium level in the supernatant.

Phosphorus removal was increased by all levels of magnesium addition. COD removal was best with no magnesium addition and lowest with the highest magnesium supplement.

The addition of magnesium thus appeared to increase the reduction of certain components; but very high levels of magnesium tend to reverse this effect. The only parameter adversely affected by magnesium appeared to be COD reduction. There seems to be no satisfactory explanation for this observation.

3.15 Heavy Metal Removal at High pH

A number of publications indicate that lime treatment is an ideal method for the removal of heavy metals (see Appendix C). The addition of various heavy metals to raw sewage prior to lime treatment has already been investigated but was considered sufficiently important to warrant verification of its efficiency in one of the wastewaters used in this study.

TABLE 13

Effect of High pH with and without Magnesium Supplements in
Treatment of Soft Ottawa City Wastewater.

Sample Treatment	Settled Solids		Susp. solids in Supernat- ant (mg/l)	Total PO ₄ (mg/l as P)	Turbidity J.T.U	COD (mg/l)	Ca ⁺⁺ (mg/l)	Mg ⁺⁺ (mg/l)
	Sludge Volume mg/l	Sludge OD wt. (mg/l)						
Control	2	-	60	5.20	32.5	86	54.7	11.3
pH 11.5 †	32	0,340	8 (87)	.42 (92)	1.40	38 (56)	66.8	1.3
pH 11.5 + 5 mg/l Mg ⁺⁺	34	5,985	6 (93)	.08 (98)	.64	69 (20)	46.3	1.2
pH 11.5 + 10 mg/l Mg ⁺⁺ *	33	7,140	6 (93)	.24 (95)	.55	60 (30)	82.0	1.7
pH 11.5 + 20 mg/l Mg ⁺⁺ *	44	5,595	15 (75)	.09 (98)	.25	65 (24)	70.7	1.6
pH 11.5 + 40 mg/l Mg ⁺⁺ *	52	6,155	10 (83)	.08 (98)	.27	57 (33)	76.7	2.4
pH 11.5 + 100 mg/l Mg ⁺⁺ *	68	6,240	22 (63)	.21 (96)	.51	89 (0)	82.5	5.6

- Supernatant analyses were determined one hour after the effluent was adjusted to pH 8.5 by carbonation.

() Data in parenthesis are percent reduction.
Total alkalinity of wastewater 139.5 mg/l as CaCO₃

* Mg⁺⁺ added as MgCl₂

† Lime dose of 330 mg/l.

The addition of various metals to Beaconsfield wastewater was investigated at two levels, i.e. 10 and 100 mg/l. The treatment consisted of lime addition to pH 11.5 supplemented with 30 mg/l magnesium. In addition, a treatment was carried out at pH 9.5 supplemented by 30 mg/l magnesium on wastewater to which 100 mg/l heavy metal had been added (Table 14).

The measured levels of heavy metal in solution before and after the addition of lime were used for calculating the reduction. Chromium showed very little reduction; lead and selenium showed approximately 50% reduction; copper, nickel and zinc were almost completely removed.

The actual concentrations of heavy metal prior to the addition of lime in the 100 mg/l supplement series were not determined, hence, percent reductions were not calculable. Regardless of this shortcoming, the same trend in removal was observed at pH 11.5 whether 10 or 100 mg/l of heavy metal was added. There was little difference in residual heavy metals whether the water was adjusted to pH 11.5 or 9.5, except for selenium.

3.16 Post Carbonation Precipitation

During a number of carbonation trials, it was noted that, with overnight storage, a fine precipitate settled out on the bottom of the flask. Presumably this was related to the rate of carbon dioxide addition as noted by Culp et al (7). A number of experiments were carried out to determine if this precipitate contained phosphorus which would normally be discharged to the river because of insufficient time to precipitate out. Prior to carbonation to pH 7.8, the wastewaters were pH adjusted to 10.0 or 11.5 with and without sludge recycle. The phosphorus content of the supernatant was determined before and after vigorous agitation. Agitation was used to resuspend the fine precipitate and aliquots were immediately withdrawn to ensure representative sampling of the resuspended precipitate.

The results shown in Table 15 indicate that additional phosphorus is precipitated on carbonation of the effluent from the lime precipitation stage. Thus, phosphorus is presumably present as calcium phosphate and, as such, may not be readily available to most biological systems.

TABLE 14

Effect of High pH on Heavy Metal Removal in
Beaconsfield Wastewater

HEAVY METAL	Heavy Metal Addition of approx. 10 mg/l		Heavy Metal Addition of approx. 100 mg/l	
	Residual (mg/l) of heavy metal after -		Residual (mg/l) of heavy metal after -	
	No treatment (control)	Ca(OH) ₂ to pH 11.5 + 30 mg/l Mg ⁺⁺	Ca(OH) ₂ to pH 9.5 ² + 30 mg/l Mg ⁺⁺	Ca(OH) ₂ to pH 11.5 + 30 mg/l Mg ⁺⁺
Copper (CuSO ₄)	1.7	0.18 (89)	0.26	0.30
Chromium (K ₂ CrO ₄)	8.4	7.3 (13)	77.0	65.0
Lead (Pb(NO ₃) ₂)	1.1	<0.5 (>50)	<0.5	<0.5
Nickel (NiSO ₄ ·6H ₂ O)	9.4	0.2 (98)	1.6	0.6
Zinc (ZnSO ₄ ·7H ₂ O)	1.4	<0.02 (<98)	0.02	<0.02
Selenium (H ₂ SeO ₃)	7.7	3.4 (56)	4.8	22.5
Cadmium (CdCl ₂ ·2-1/2 H ₂ O)	4.3	<1 (77)	1.0	<1

* All samples settled for one hour prior to supernatant analysis.

- Mg⁺⁺ added as MgCl₂·6 H₂O

- () data in parenthesis are percent removal.

TABLE 15

Amount of PO_4 - P in Post Carbonation Precipitation After 18 Hours

	Lime Addition to pH --	PO_4 - P in carbonated super- natant after settling 18 hrs. (mg/l)	PO_4 - P in carbonated super- natant after settling 18 hrs. then shaken to resuspend precip- itate (mg/l)	Amount of PO_4 - P in post precipitate (mg/l)
Untreated Effluent	-	5.0	5.4	0.4
No Sludge Recycle	10.0	0.94 (81)	1.08	0.14 [13]
	11.5	0.08 (98)	0.18	0.10 [51]
With 10% sludge recycle	10.0	1.02 (80)	1.20	0.18 [15]
	11.5	0.16 (97)	0.22	0.06 [27]

All samples carbonated to pH 7.8

() Data in parenthesis are percent reduction

[] Data in brackets are percent of total amount of phosphate
(soluble and precipitated).

From these results, it appeared that even further phosphorus reduction could be achieved by ensuring proper carbonation reaction times and sequences, thereby avoiding post carbonation precipitation. The possibility of using iron coagulants to aid in clarification after carbonation should be further explored. However, it is believed that the small amount of phosphorus escaping in this fashion is insignificant except where ultra pure effluents are required. This post precipitation could, however, clog and blind activated carbon units.

The cost of carbonation will depend on the size of the system, the carbonating method used, and the alkalinity of the water and would vary with each municipality.

3.17 Studies at Red Rock - A Soft Water Area

The experimental results from jar testing using hard and moderately hard water indicated that lime treatment alone was sufficient to produce a good quality effluent. Further studies were undertaken to ascertain if equally good results could be obtained with soft water.

3.17.1 Effect of pH on Red Rock Wastewater Quality

Jar tests were carried out on composite samples collected between 7:00 and 9:30 am. Samples were pH adjusted between 9.5 and 11.5, as shown in Table 16. Duplicates of these treated samples were further supplemented with 30 mg/l magnesium or with 30 mg/l magnesium plus 5 mg/l iron. It should be noted that low activity (old) calcium hydroxide containing 36% calcium carbonate was inadvertently used in this study. Consequently, all calcium hydroxide dose levels reported in this section would have been correspondingly smaller if fresh calcium hydroxide had been used. All samples were carbonated to pH 8.0 with compressed carbon dioxide.

With increasing pH there was a decrease in suspended solids, turbidity, COD, bacterial reduction and a less pronounced phosphorus removal. Accompanying the increased lime dose and the addition of supplements was a corresponding increase in sludge volume (Table 16). The addition of magnesium caused a distinct reduction in suspended solids, and a slight increase in turbidity. However, the simultaneous addition of iron and magnesium salts improved both suspended solids and turbidity reduction (Table 16).

TABLE 16

RED ROCK MUNICIPAL EFFLUENT

Effect of pH and Mg^{++} on Wastewater Treatment

Sample Treatment	Ca(OH) ₂ Addition mg/l*	Vol. (ml) of settled solids in Imhoff cone after ... mins					Susp. Solids mg/l	Turb- idity JTU	COD mg/l	Total PO ₄ mg/l as P	Total Coliforms per 100 ml	BOD ₅ mg/l
		5	10	20	45	60						
Untreated raw sewage (pH 7.7)	0	0	0	0	0	0	55	26 (tap water 7.5)	75	2.8	4.5×10^6	40
Ca(OH) ₂ to pH 9.5 settled 1 h, decanted and carbonated to pH 8	100	1.5	2	3	3	3	40 (27)	27	56 (25)	1.6 (43)	2.0×10^6	
Ca(OH) ₂ to pH 10.5 settled 1 h, decanted and carbonated to pH 8	200	6	6	6	5	5	25 (55)	12.5	30 (60)	0.48 (83)	1.2×10^5	
Ca(OH) ₂ to pH 11.0 settled 1 h, decanted and carbonated to pH 8	250	15	13	12	11	10	20 (64)	6.2	26 (65)	0.34 (88)	8.0×10^1	
Ca(OH) ₂ to pH 11.5 settled 1 h, decanted and carbonated to pH 8	330	25	25	22	20	19	10 (82)	3.9	19 (75)	0.14 (95)	nil	30**
Ca(OH) ₂ to pH 11.5 + 30 mg/l Mg^{++} settled 1 h, decanted and carbonated to pH 8	330	42	40	37	34	32	5 (91)	4.9	19 (75)	0.34 (88)	nil	
Ca(OH) ₂ to pH 11.5 + 30 mg/l Mg^{++} + 5 mg/l Fe^{++} settled 1 h, decanted and carbonated to pH 8	330	46	45	40	38	36	5 (91)	2.8	33 (56)	0.10 (96)	N.S.	

- Analysis after 1 h settling and carbonation, except for sludge volumes
- Data in parenthesis are percent reduction
- Alkalinity: 65.4 mg/l as CaCO₃

* Low quality lime. Tested at 64% Ca(OH)₂.

** A BOD₅ of 29 ppm was attained in settling column tests under these conditions.

N.S. = not sampled.

Of interest also is the total elimination of coliforms at pH 11.5 and the reduction of BOD_5 by 50%, from 60 mg/l to 30 mg/l, at pH 11.5. Figure 8 illustrates the decrease in suspended solids at various pH levels with a corresponding increase in sludge volume. The gain in suspended solids removal at pH 11.5 with the addition of coagulant aids is somewhat offset by the marked increase in sludge volume.

3.17.2 Effect of Various Magnesium Levels on Red Rock Effluent at pH 11.5

Since the addition of lime to pH 11.5 appeared to be the best treatment, and since magnesium seemed to have a beneficial affect (3.17.1) it was decided to further explore the effect of magnesium at pH 11.5 on the Red Rock effluent.

All samples received the same addition (330 mg/l activity 65%) of calcium hydroxide, to which various levels of magnesium were added, ranging from 0 to 60 mg/l.

The data presented in Table 17 shows the effect of increasing additions of magnesium chloride on the pH response to the lime addition. Because of this simultaneous variation in pH and magnesium content it was not possible to make a direct comparison of the samples.

In spite of these two variables, some interesting observations were made from these experiments. At low magnesium additions, 0, 5, and 15 mg/l, all samples exhibited similar turbidity (4.2 JTU), similar suspended solids, and similar phosphorus removal, whereas COD removal and sludge volume increased quite noticeably with increased magnesium. A comparison of these samples at constant pH was not made but, based on previous experiments, turbidity and suspended solids might be expected to decrease.

The very high COD reduction, especially when supplemented with 15 mg/l of magnesium (from 8.2 to 7.0), the low absorption (from 3.7 to 0.1 mg/l) and suspended solids level, the elimination of coliforms and the sparkling low turbidity waters surpassed the performance of many sophisticated and expensive systems.

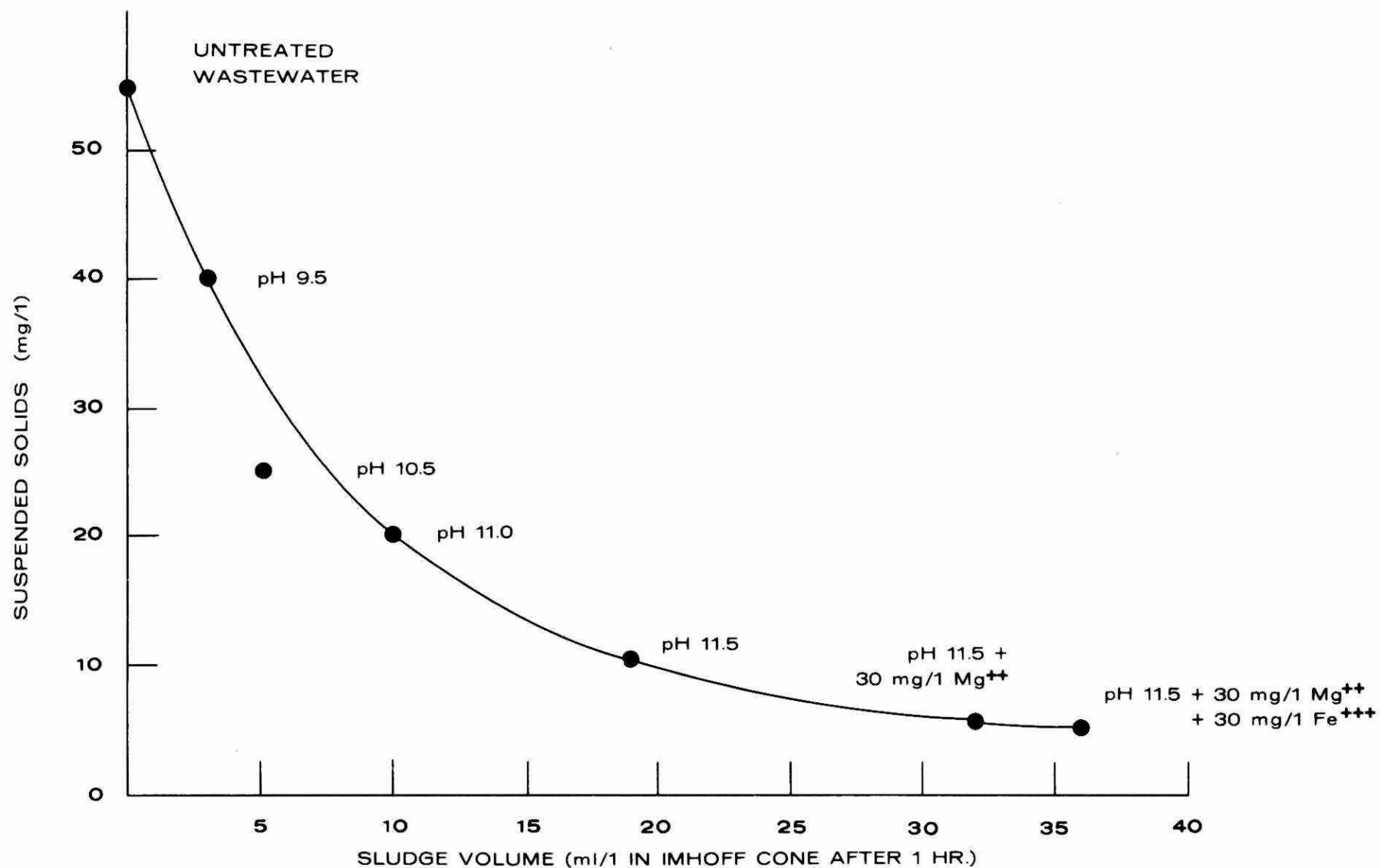


Figure 8 Interdependency of Sludge Volume, Suspended Solids, pH, and Coagulant Aid.

TABLE 17

RED ROCK MUNICIPAL EFFLUENT
Effect of Mg^{++} in Wastewater Treatment at pH 11.5

Sample Treat- ment	Sludge Vol (ml.) in Imhoff cone after ... mins					Turbidity (JTU) after settling for mins					Solids (mg/l)			Calc. Sludge consist. after 1 h	Total PO_4 as P (mg/l)	pH immed. prior to carb.	pH after carb.	Turb. immed after carb	Turb. 1 h after carb.	COD after carb.
	5	10	30	45	60	5	10	30	45*	60	Susp.	Diss.	Tot.							
Raw Sewage	very light					31	31	31	31	31	48	410	438	0	3.7	7.6	-	-	-	82.
Mg^{++}																				
0 mg/l	26	24	20	19	19	28	15	7.6	6.5	4.2**	23	405	428	1.9	0.20 (95)	11.4	7.3	5.2	1.1	18 (78)
5 mg/l	27	26	23	22	21	27	19	7.2	4.3	4.3	20	435	455	1.7	0.22 (94)	11.2	7.3	7.0	1.2	10.5 (87)
15 mg/l	39	35	32	32	31	24	16	4.9	3.3	4.2	22	470	492	1.2	0.24 (94)	11.2	7.2	6.9	1.2	7.0 (91)
30 mg/l	45	41	39	40	40	22	17	6.0	2.4	3.6	30	575	605	0.8	0.12 (97)	11.0	7.3	7.3	0.91	14.0 (83)
60 mg/l	45	41	40	40	33	20	-	6.9	6.4		27	725	752	0.7	0.10 (97)	10.7	7.0	9.5	0.73 **	24.6 (70)

- Mg^{++} added as $MgCl_2 \cdot 6 H_2O$

- 330 ppm $Ca(OH)_2$ required for pH 11.5 adjustment (activity 65% as $Ca(OH)_2$).

* Supernatant gently stirred after 45 mins to detach flock from walls.

** Tap water JTU value: 7.5

() Data in parenthesis are percent reduction.

3.17.3 Relation Between Duration and Rapid Mixing and Setting Rates

Previous work on Beaconsfield wastewaters had indicated that a short rapid mix followed by a longer slow mix gave the most rapid settling sludge and the clearest effluent. A similar study was undertaken on Red Rock effluent to obtain preliminary data for the design of a clarifier for this type of sludge.

Contrary to what has been previously observed (3.13), longer rapid mixing times (16 min) gave the clearest effluent and one of the best settled sludges (Table 18). A possible explanation for this difference is the amount of magnesium present in the effluent. Thompson et al (19) reported that short rapid mixing time was sufficient to produce a good sludge and clear effluent in the presence of magnesium. The Beaconsfield effluent had a natural magnesium content of 29 mg/l whereas the Red Rock effluent contained only 4.8 mg/l.

The effect of magnesium levels on mixing times and mixing speeds should be re-examined to clarify these apparently contrary results.

3.17.4 Settling Tests for Clarifier Design

In order to test the settleability of the Red Rock lime sludge, ten gallons of wastewater were adjusted to pH 11.5 by flash mixing with lime for two minutes, then stirring slowly with a paddle mixer for a further 13 minutes. The mixture was then poured into an 8 foot by 8 inch (2.44 m by 20 cm) Plexiglas cylinder and allowed to settle. Sampling ports at every foot permitted the removal of samples at various depths and at various times.

Because of the possibility that the Plexiglas might develop an electrostatic field and thus affect the settling rate of the sludge particles a parallel experiment was carried out in an 18" (46 cm) diameter steel drum.

The results of the two settling column tests performed on flocculated Red Rock townsite sewage are shown in Table 19.

Initial settling rates in the 8" Plexiglas column were very rapid; 75% of the flocculated solids were removed in twelve minutes. However, solids removal beyond 90% required considerably longer retention

TABLE 18

RED ROCK MUNICIPAL EFFLUENT

Effect of Rapid Stirring on Settling Rate

Length of rapid stir (100 rpm) in jar test. All samples slow stirred (30 rpm) for 5 min	Vol. (ml) of settled solids in Imhoff cone after ... min						Turbidity (JTU) after mins at pH 11.5					
	5	10	15	30	45	60	5	10	15	30	45*	60
16 min	22	19	18	16	15	15	30	-	7.5	5.0	5.2	4.9
13 "	24	22	20	18	17	17	19	-	7.5	5.3	5.4	6.3
10 "	21	19	18	17	15	15	18	-	11	6.7	6.5	7.8
7 "	20	18	18	16	15	15	22	-	15	7.7	7.8	8.1
4 "	23	21	19	17	16	16	34	-	18	8.7	8.7	8.7
1 "	0	10	10	10	9	9	52	-	33	16	17	13

* Supernatant gently stirred after 45 min to release particles clinging to vessel wall.

TABLE 19

Clarifier Performance Data Derived from Settling Tests

Test #1 Untreated suspended solids 50 mg/l
 (Plexiglas Flocculated solids 430 mg/l
 Column) Ca(OH)₂ added 333 mg/l*

Residence Time mins.	Settling Velocity ft/min	Rise Rate GPD/ft ²	% Solids Removal	Residual Solids mg/l
5.5	1.085	11,700	57.1	184
8.0	0.740	7,970	69.2	132
11.5	0.52	5,600	77.4	97
33	0.18	1,940	91.5	37
105	0.056	600	95.8	18
130	0.046	490	96	17

Test #2 Untreated suspended solids 61 mg/l
 (Steel Drum) Flocculated solids 458 mg/l
 Ca(OH)₂ added 333 mg/l*

Residence Time mins.	Settling Velocity ft/min	Rise Rate GPD/ft ²	% Solids Removal	Residual Solids mg/l
8	0.74	7,970	60	183
12	0.49	5,280	75.4	113
16	0.37	3,980	83.7	75
25	0.24	2,580	91.3	40
117	0.051	550	95.8	19
150	0.039	420	96	18

* Available Ca(OH)₂ is 64%

time. Based on this column settling data, it appears that a theoretical residence time of approximately 110 minutes would be required to achieve a residual solids level of less than 20 mg/l.

Additional testing in an 18" diameter steel drum indicated that settling in the 8" I.D. column may have been hindered by electrostatic fields associated with the Plexiglas walls. The test data from the drum indicated that 20 mg/l residual solids could be achieved with a theoretical residence time of 40 minutes. Further settling tests would be necessary to determine more precisely the effluent's clarification characteristics.

Sludge samples were collected from the two settling column tests. Sludge per cent solids for the two tests were 4.8% and 3.6% respectively, and amounted to 0.5% and 1.0% of the effluent volumes treated.

Preliminary sludge dewatering tests using an Eimco leaf filter indicated that 60 seconds form time and 120 seconds drying time would produce a cake of 26% solids. The indicated filter throughput of 2.7 lb/ft²/hr (13.18 kg/m²/hr) would require a filter size of less than 20 ft² (1.86 m²) for a town the size of Red Rock.

Based on the results of the present investigation, the following conclusions have been drawn:

- (1) The addition of lime to pH 9.0 did not consistently remove 80% phosphorus, as reported by some authors. The minimum pH required to achieve good (approximately 1 mg/l) phosphorus removal appeared to be 9.5 - 10.0 and excellent (less than 1 mg/l) phosphate reduction was obtained at pH 11.0 - 11.5.
- (2) The addition of lime to a higher pH such as 11.0 - 11.5 produced an effluent with most of its contaminants removed e.g.
 - a) COD removals as high as 80% were observed.
 - b) Most suspended solids were removed, and, if properly carbonated levels of less than 15 mg/l were obtained. The effluent turbidity often fell below 1.0 Jackson Turbidity Units.
 - c) BOD reductions were of approximately equal magnitude to those observed for COD.
 - d) All coliform bacteria were destroyed at a pH of 11.5 during a contact period of 1 hour. Zero coliform discharge from a conventional treatment plant would require massive chlorination.
- (3) Phosphate reduction did not appear to be improved by magnesium addition, regardless of the magnesium content of the water.
- (4) Magnesium additions enhanced the reduction of most contaminants when the initial magnesium content was less than 10 mg/l.
- (5) Iron salts aided in turbidity reduction in the carbonation step.
- (6) The amount of calcium carbonate precipitated during carbonation was variable, depending on the rate of carbonation, the pH to which the effluent was carbonated, and the alkalinity of the effluent prior to carbonation.
- (7) Sludge recycle aided in the reduction of some contaminants but often increased the turbidity. Sludge recycle also appeared to decrease the stirring time required to obtain maximum solids removal.

- (8) Optimum flash mix times and speeds during jar testing appeared somewhat variable. This was tentatively attributed to the amount of magnesium in the sludge.
- (9) Preliminary studies indicated that primary recalcination is feasible.
- (10) Lime treatment should produce an effluent almost equivalent to conventional secondary treatment, unaffected by upsets, surges, or temperature. The cost should be less than primary-secondary treatment, and substantially less than primary-secondary-tertiary systems.

ACKNOWLEDGEMENT

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APPENDIX A

PRELIMINARY CALCINATION STUDIES OF
LIME SLUDGE FROM WASTEWATER TREATMENTS

APPENDIX A

PRELIMINARY CALCINATION STUDIES OF LIME SLUDGE FROM WASTEWATER TREATMENTS

Since jar tests do not produce sufficient sludge for calcination studies, a lime sludge produced at the Newmarket, Ontario waste treatment plant was used in one of the calcination tests. The Newmarket wastewater is only treated with lime to a pH of 9.5, and it would differ considerably from a sludge produced at pH 11.5 since the ratio of CaCO_3 to organic matter increased with increasing lime dosage. However, it was believed that an evaluation of the Newmarket sludge would provide some indication of the incineration and calcination behaviour of lime sludges in general.

The autoclaved Newmarket sludge was dried at 120°C and examined under a stereo microscope. It was found to contain a significant fibre fraction, quartz, clay, calcite, and a mixture of unidentifiable minerals. Chemical analysis of the sludge yielded the following data:

Total solids	(% at 105°C)	9.1
Ash	(% of solids)	64.1
CaCO_3	(% of ash)	84.1
Acid Insols	(% of ash)	9.2

X-ray diffraction revealed the major fraction to be calcite with a smaller amount of quartz and lesser quantities of unidentifiable materials present. X-ray fluorescence for $Z > 12$ showed a large amount of Ca, significant Si, and smaller portions of K, Fe, S, and Cl_2 with traces of Ti.

Qualitative experiments with small amounts of the dry solids showed that the calcite would calcine but that it would flux to some extent. Accordingly, a program for gentle calcination was evolved using minimum temperature but yielding complete carbon burnout. The dry sludge was broken into 1/2" pieces, placed in an incolen tray, and the temperature increased at the rate of 350° one hour to 950°C where it was held for one hour. At the end of this time, the calcine was immediately removed from the furnace and cooled. The resulting calcine was a medium buff colour and was entirely free of carbon or other organic material and analysed 93% CaO .

The relatively large amount of quartz and clay material is a potential problem area and methods of removing this material prior to recycling the lime will have to be developed. Further work is also required to optimize calcination conditions.

Forty-five gallons (Imp.) of Beaconsfield wastewater were treated with lime to a pH of 11.5 and the sludge recovered for calcination experiments. The sludge was calcined exactly as described above. To determine how completely the sludge samples had been calcined, samples of Beaconsfield and Newmarket calcine were left in the furnace at 900° C over a weekend and then analysed for available CaO with the following results:

Calcined sludge, Newmarket, Ont.

"Available lime", as % CaO	50.7
"Available lime", as % CaO after calcination at 900° C for 72 hr	50.4
X-ray diffraction	CaO with a small amount of Ca (OH) and other unidenti- fied compounds.

Calcined sludge, Beaconsfield, Que.

"Available lime" as % CaO	35.1
"Available lime" as % CaO after calcination at 900° C. for 72 hr	66.9
X-ray diffraction	CaO with CaCO ₃ and small amounts of unidentified compounds.

As a check on the method for "available lime", the following synthetic mixtures were tested. The lime used was first calcined at 900° C for 72 hours.

Wt. CaO taken (g)	Wt. CaCO ₃ taken (g)	Wt. Ca ₃ (PO ₄) ₂ taken (g)	Wt. CaO found (g)	"Available lime" as % CaO
0.3989	-	-	0.3707	92.9
0.3954	0.0976	-	0.3655	92.4
0.3495	0.0983	0.0526	0.3204	90.7

These results give a mean value of 92.3% with a range of ± 0.6%.

Since it was conceivable that Red Rock could use some of the calcined lime mud from the adjacent pulp and paper mill, the material was analysed. As shown below the lime was sufficiently good for waste-water treatment. Similarly, a sample of Cornwall calcined lime was analysed. The difference in "available lime" may be due to the difference in the kilns used as well as the different processes employed at the two mills.

Calcined Lime Mud, Cornwall and Red Rock

Red Rock, Ont.

"Available lime" as % CaO	79.5
X-ray diffraction	CaO with possibly a small amount of MgO

Cornwall, Ont.

"Available lime" as CaO after calcination at 900°C over weekend	51.4
X-ray diffraction	CaO with possibly CaSO ₄ and Na ₂ SO ₄

Conclusion

This work has shown that a large portion of the lime can be recovered, however, more work would be required to optimize calcining conditions and to evolve methods for sand and clay removal. Failure to do so would result in the formation of calcium aluminates and/or calcium silicates being formed during calcination which would greatly reduce the "available lime".

APPENDIX B

pH RESPONSE TO LIME ADDITION -
PINCOURT, BEACONSFIELD AND RED ROCK
WASTEWATER

APPENDIX B

The pH response to lime addition to the Pincourt, Beaconsfield and Red Rock wastewater are presented in Figures B1, B2 and B3.

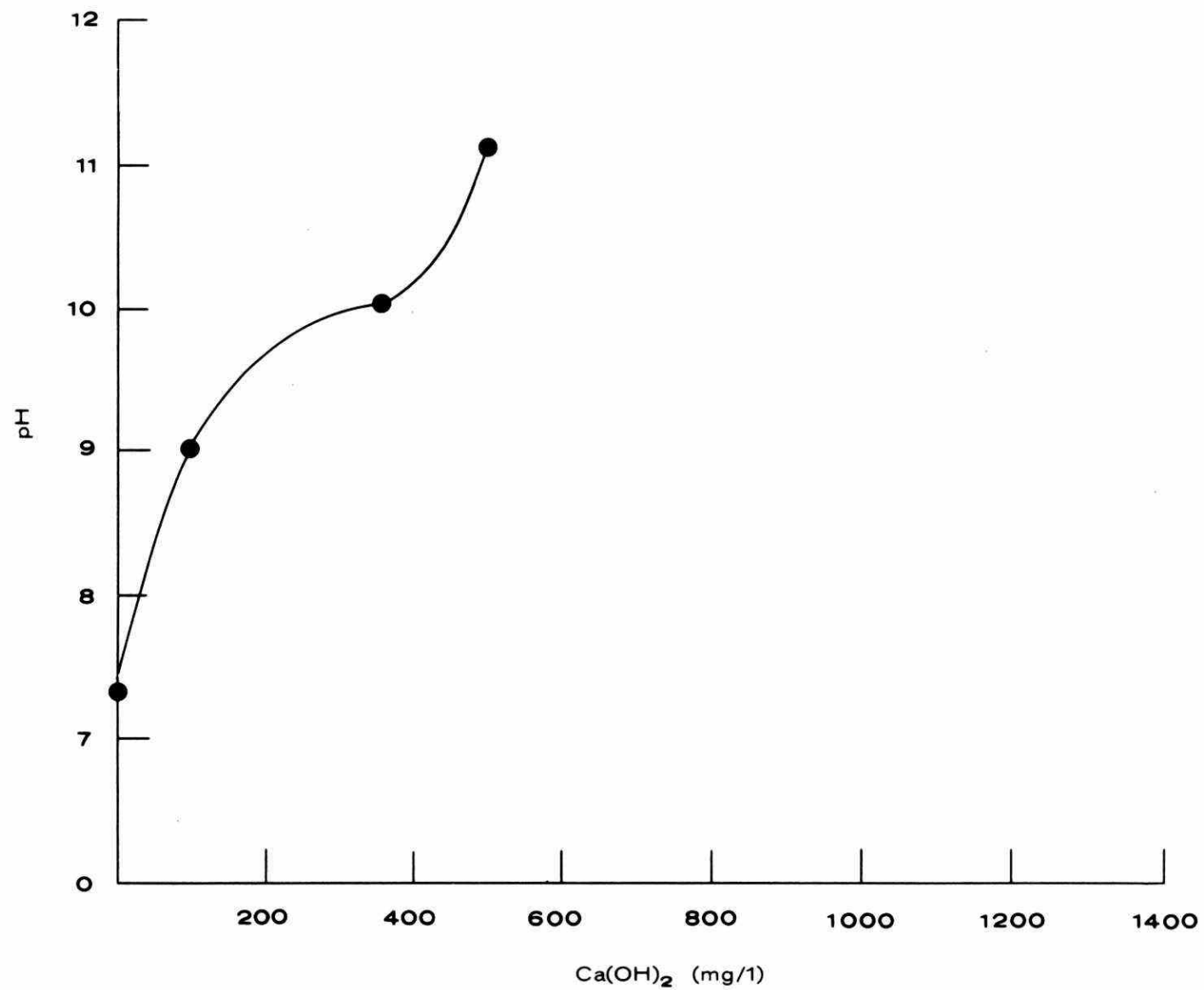


Figure B1 PINCOURT pH Response of Wastewater to Lime Addition.

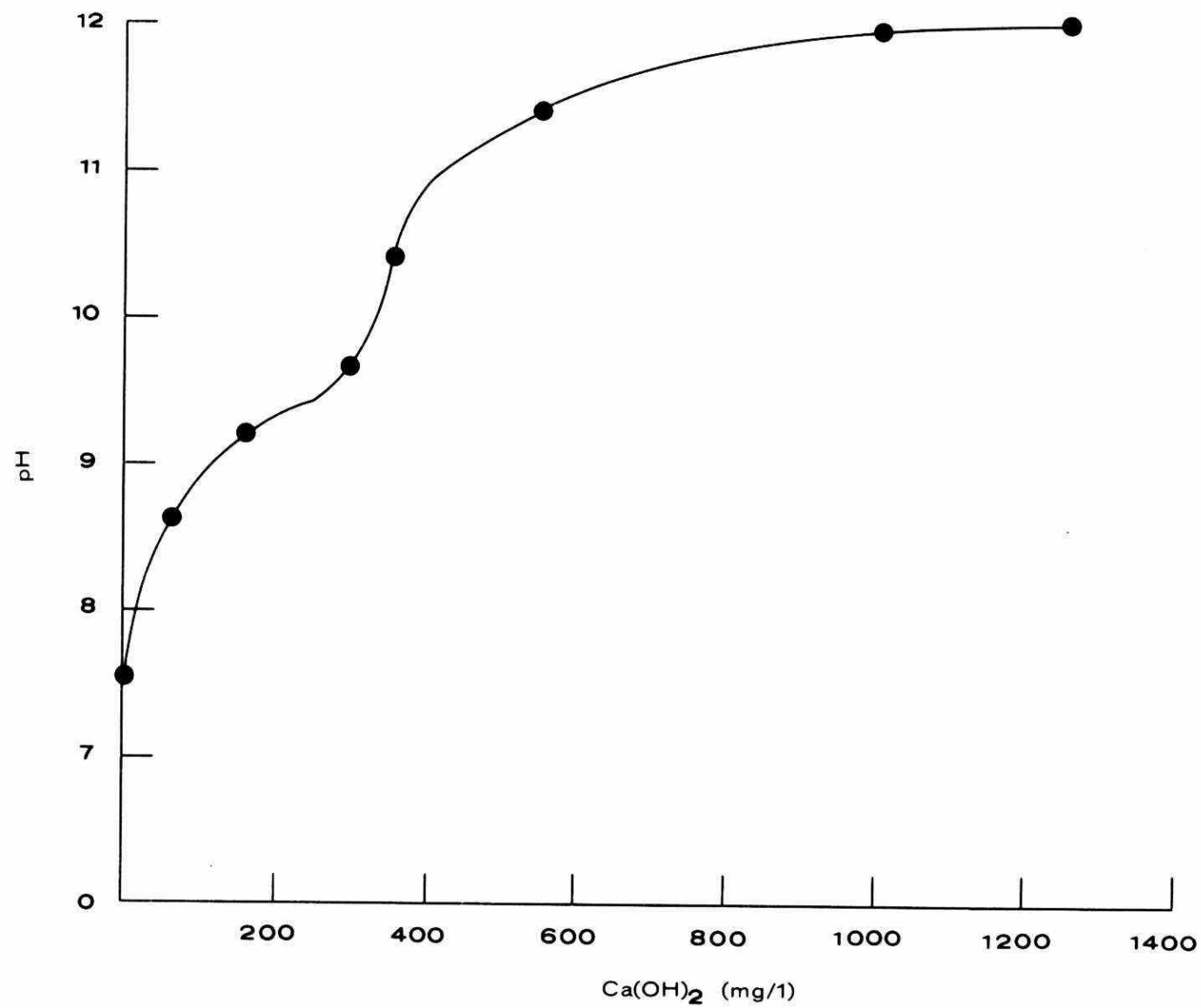


Figure B2 BEACONSFIELD pH Response of Wastewater to Lime Addition

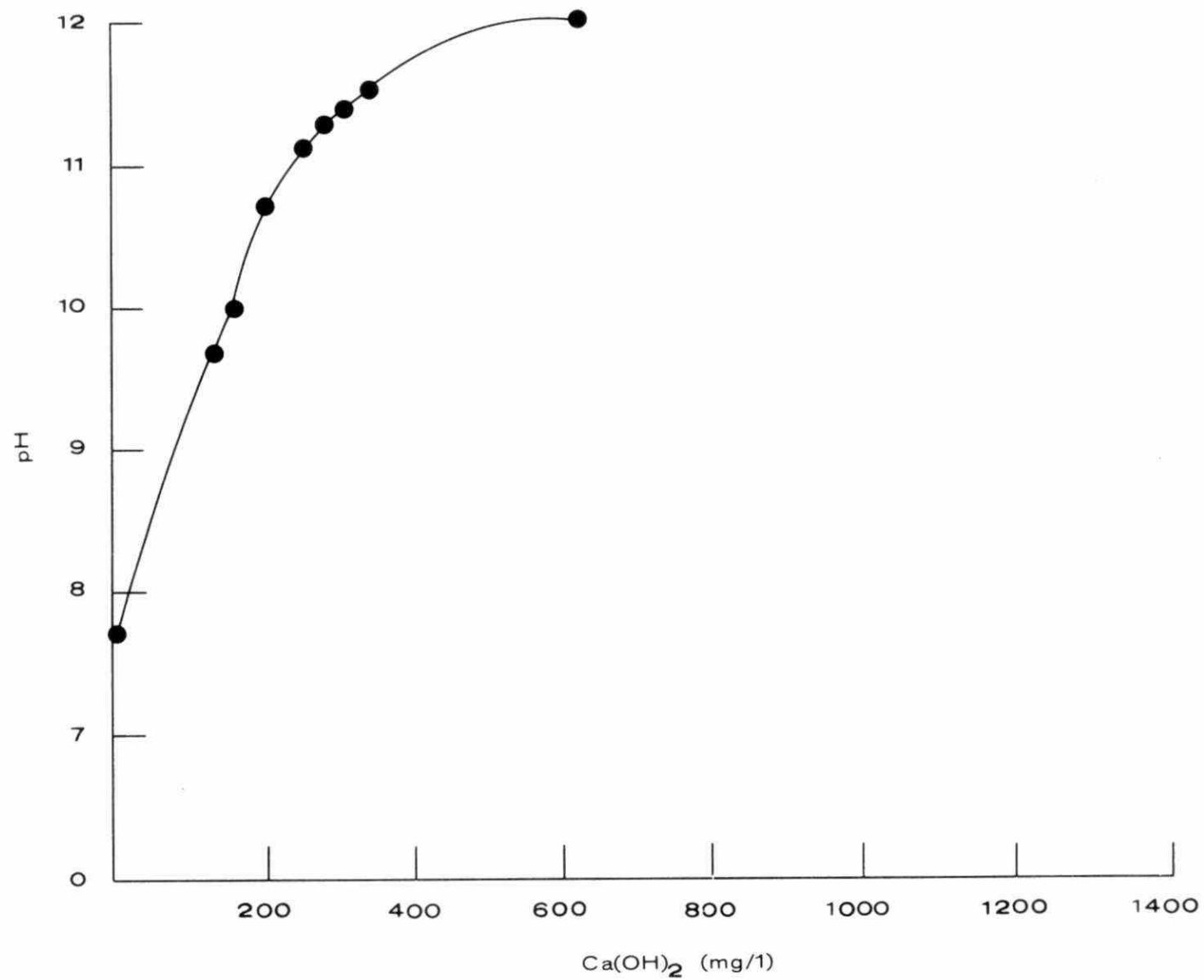


Figure B3 RED ROCK pH Response of Wastewater to Lime Addition

APPENDIX C

LIME TREATMENT OF MUNICIPAL
WASTEWATERS - A LITERATURE REVIEW

CONTENTS

	<u>Page</u>
PREFACE	71
C1 CHEMICAL REACTIONS	72
C1.1 Bicarbonate Reduction	72
C1.2 Phosphate Precipitation	73
C1.3 Organic Phosphorus Removal	75
C1.4 Magnesium Hydroxide as a Coagulant	75
C1.5 Nitrogen Removal	80
C1.6 Organic Acid Neutralization	80
C1.7 Heavy Metal Removal	80
C2 LOW pH TREATMENT OF WASTEWATER	85
C2.1 Chemical-Biological-Anaerobic Digestion	85
C2.2 Chemical-Biological Incineration	85
C2.3 Chemical-Biological Recalcination	87
C2.4 Kinetics of Phosphorus Removal at Low and High pH	91
C3 HIGH pH TREATMENT OF WASTEWATER	93
C3.1 Interdependency of Calcium, Magnesium, and Phosphorus	93
C3.2 Dissolved Calcium and pH	94
C3.3 Clarification of Treated Effluents	94
C3.4 pH Adjustment in Nitrified Effluents	96
C4 CARBONATION	97
C4.1 Carbonation of Treated Effluents	97
C4.2 Carbonation of Lime Sludges	98
C4.3 Carbon Dioxide Requirements	98
C4.4 Clarifier Size	99
C5 AMMONIA REMOVAL	100
C5.1 Natural Zeolites	100
C5.2 Air Stripping	100
C6 LIME SLUDGES	102
C6.1 Land Disposal	102
C6.2 Chemical Recovery of Sludges	105
C7 LIME SLUDGE HANDLING PROCESSES	107
C7.1 Clarification	107

CONTENTS

	<u>Page</u>
C7.2 Sludge Dewatering	108
C7.3 Sludge Calcination	109
C8 LIME REQUIREMENTS	110
REFERENCES	114
SUPPLEMENTAL REFERENCES	124

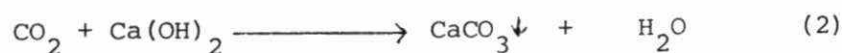
PREFACE

Lime has been used in wastewater treatment for at least twenty years (14) for the specific purpose of phosphorus removal. Though its acceptance and application as a chemical for wastewater treatment was slow, and it was, at times, rejected because of sludge handling problems, lime treatment has in recent years become a popular and relatively inexpensive method for many physical-chemical and chemical-biological systems. (References 1 to 13, 15, 16, 18, 21, 24, 30, 34, 44, 49, 51.) A supplemental reference list has been included at the end of this review for those seeking information on specific topics concerning the utilization of lime for the treatment of wastewaters.

C1 CHEMICAL REACTIONS

C1.1 Bicarbonate Reduction

The addition of hydrated lime (Ca(OH)_2) to water, either potable or wastewaters, initiates a number of reactions. One of the major lime consuming reactions is dependent on the alkalinity of the waters, and to a lesser degree, its carbon dioxide content.



At pH 10, all of the calcium bicarbonate has been converted to insoluble CaCO_3 . Hence the greater the alkalinity of the water, the greater the requirement of lime to increase the pH. The following figure taken from Mulbarger et al (23) illustrates this quite clearly.

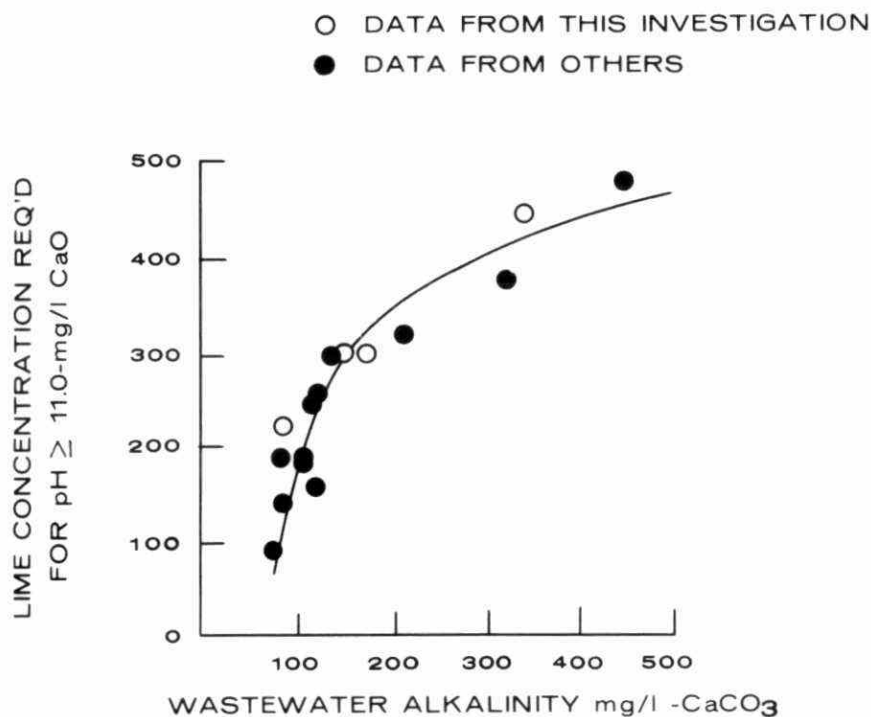


Figure C1 The Lime Dose For pH \geq 11.0 is a Function of the Wastewater Alkalinity.

Stamberg et al (20) show essentially the same phenomenon (Figure C2) but also indicate the lime requirements between pH 7 to 12.

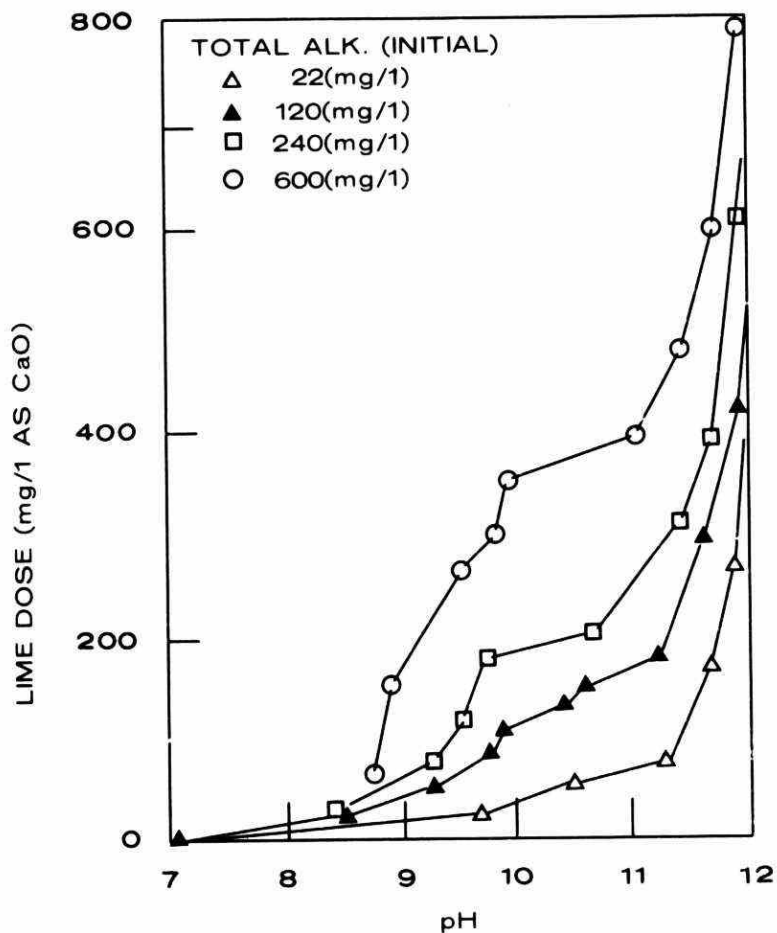
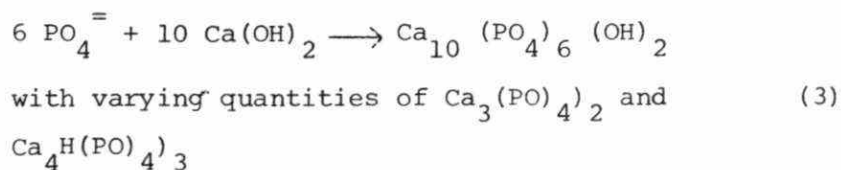


Figure C2 Alkalinity, Lime Dose, and pH.

(To convert dosage as CaO to $\text{Ca}(\text{OH})_2$, multiply by 1.393;
To Convert $\text{Ca}(\text{OH})_2$ dosage to CaO, multiply by 0.757.)

C1.2 Phosphate Precipitation

Simultaneously with the bicarbonate removal (in effect a water softening process), the phosphate ions are precipitated as a number of complexes with calcium and the hydroxyl radical, the most abundant complex being calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$).



The reaction is virtually non-reversible, and the equilibrium is to the right as the pH increases. Again the excellent work of Stamberg et al (20) is shown graphically in Figure C3.

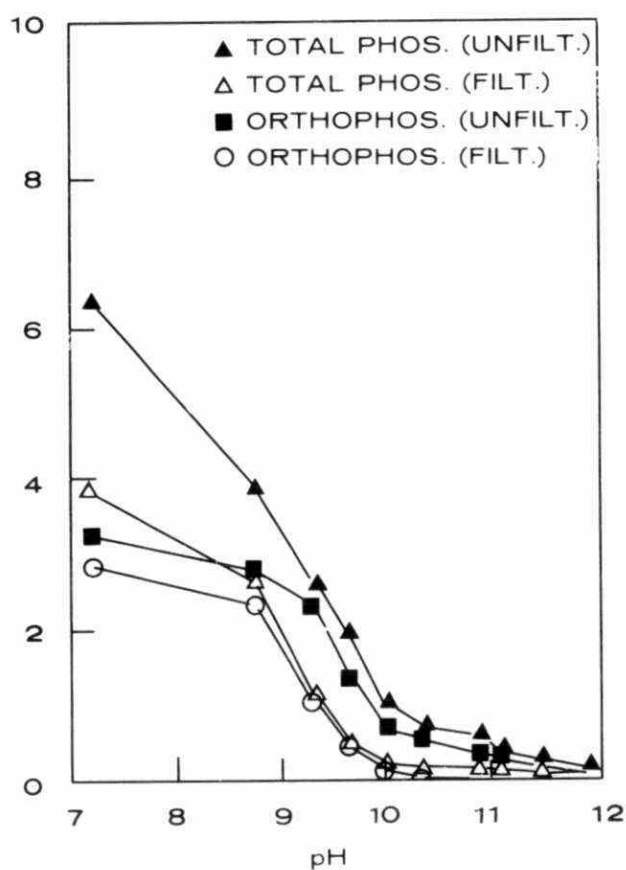


Figure C3 Lime Precipitation and Phosphorus Removal From Raw Wastewater.

It is in the mediation of this reaction that lime has been extensively employed in wastewater treatment.

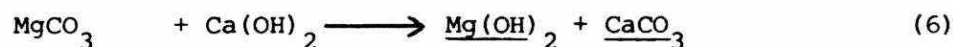
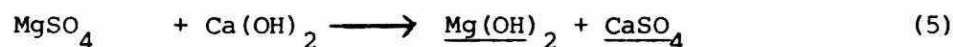
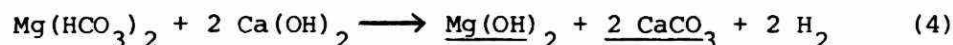
Cl.3 Organic Phosphorus Removal

Since raw wastewaters usually contain between 50% and 80% phosphorus as orthophosphate, it is necessary to explain the 95% and better removal of phosphorus by some reaction which is complementary to apatite precipitation. It appears that the metaphosphate, the tripolyphosphate and the organically bound phosphorus are removed by adsorption on the calcium carbonate or magnesium hydroxides. Further evidence (20) indicates that these complexes may be hydrolyzed to orthophosphates which in turn are precipitated as apatite.

Cl.4 Magnesium Hydroxide as a Coagulant

The consistent removal of suspended solids, and consequently the removal of organic phosphorus at high pH appears to be related to the formation of gelatinous magnesium hydroxide between pH 9.5 and 12. Hence the magnesium hydroxide serves to coagulate and precipitate particulate organics, calcium carbonate, and apatite and produce a turbidity-free supernatant solution. An important part of this present study was an attempt to elucidate and optimize the use of magnesium in the treatment of wastewaters.

The formation of magnesium hydroxide takes place above pH 9.5 in any waters which contain magnesium salts, as shown in equations 4, 5, and 6.



Even though magnesium hydroxide is a relatively insoluble product, it is not precipitated completely until pH 11 to 12 (see Figure C4 (20)).

The rapid precipitation of magnesium hydroxide between pH 11 and 12 explains the superior quality effluents obtained at pH 11.5 even though considerable phosphorus is removed at pH 9.5.

A number of coagulants or coagulant aids are available to increase the rate and quantity of suspended solids removal. The most commonly employed coagulants, because of their highly gelatinous nature,

are alum and the iron salts (usually ferrous and ferric chloride). In lime treated wastewaters, the indigenous magnesium found in the water may serve as a coagulant.

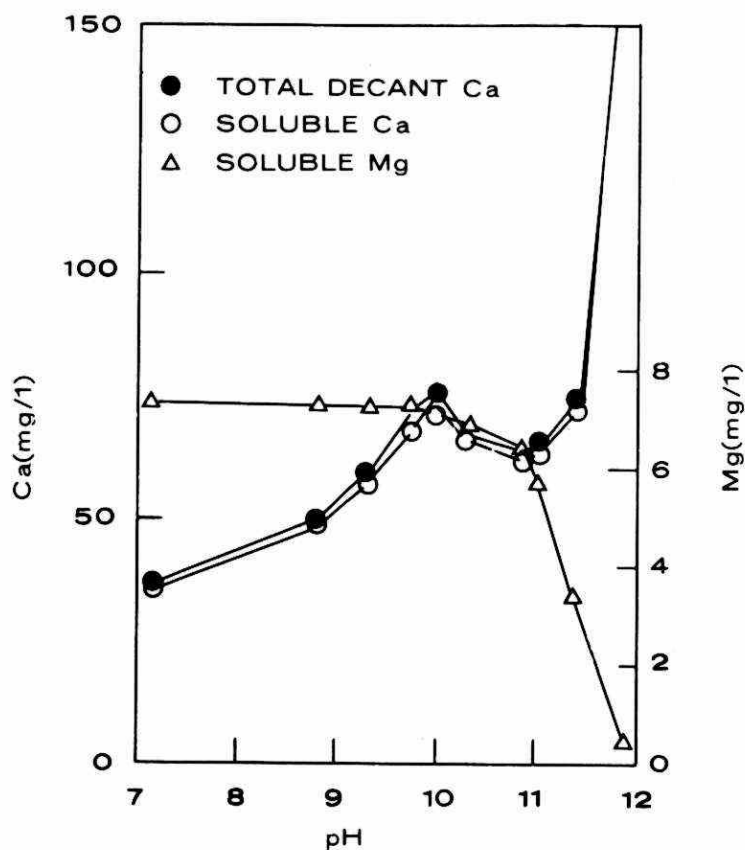


Figure C4 Lime Precipitation and Calcium and Magnesium Concentrations In Raw Wastewater.

A number of investigators have reported pronounced beneficial effects by increasing the pH to precipitate the magnesium as magnesium hydroxide, or by adding small amounts of soluble magnesium salts. Flentje (71) was perhaps the first to suggest the use of magnesium chloride as a natural coagulant when treating drinking water at high pH to remove colour, turbidity, and bacteria.

Apparently the next major publication supporting the role of magnesium as an important and efficient coagulant was by Lecompte (43). He was able to substantially improve pulp mill effluents by using lime and magnesium.

The work of Marske et al (11) at Salem, Oregon clearly demonstrates that 15 to 20 mg/l of magnesium resulted in a marked improvement in the effluent quality of a combined municipal, fruit and vegetable processing plant. As revealed in Table C1, they found that with the addition of magnesium, less calcium oxide was required to achieve the same effect. Table C2 taken from the same authors shows what lime treatment accomplished by itself, with and without magnesium addition (under "lime-recarbonated effluent").

A.P. Black and co-workers from the University of Florida developed an ingenious system for the recycling of magnesium in water treatment. Their studies led them to conclude that magnesium was extremely important in the removal of suspended solids, colour, and turbidity. Part of the improvement brought about by magnesium was its effect on the zeta potential of the suspended solids and their electrophoretic mobility (42).

Since calcium carbonate is negatively charged in water, it is neutralized by the positive charge on the magnesium hydroxide, which therefore helps to coalesce the two flocs to produce a heavy, rapidly settling calcium carbonate laden magnesium hydroxide gel. Moreover, the absorption of the two flocs decreases the negative mobility of calcium carbonate and aids in settling and dewatering. Contrary to a widely held misconception, the lime sludge containing magnesium hydroxide (even though magnesium hydroxide is very gelatinous) is easy to dewater. It aids in vacuum filtration, and is far easier to handle than regular biological sludge.

Stamberg et al (20) carried out a series of experiments to determine the effect of lime addition on phosphorus content of wastewaters. They found that calcium carbonate increased floc densities accounting for the high overflow rates, but improved clarification and liquid-solids separation was possible with as little as 5 to 10 mg/l of magnesium. Turbidities of less than one JTU were also attributed to the beneficiating effects of magnesium hydroxide.

Mulbarger (23), in an excellent paper dealing with lime sludge recalcination and recycle, assumed that high magnesium hydroxide would hinder the sludge thickening characteristics. However, experimental evidence of Black (25), Thompson (41), Stamberg (20), Lecompte (43), Albertson (17), O'Farrell (18), and Tofflemire (30) indicated improved settling and dewatering.

TABLE C1

EFFECT OF MAGNESIUM ON LIME CLARIFICATION*

T/F BOD LOADING 340-570 mg/l
SEPT. 9 - SEPT. 22

LIME DOSE mg/l CaO	MAGNESIUM DOSE mg/l Mg	RECARBONATED EFFLUENT COD		RECARBONATED EFFLUENT TOTAL TSS		RECARBONATED EFFLUENT ORGANIC SS	
		mg/l	% REM	mg/l	% REM	mg/l	% REM
503	0	115	54	42	83	18	89
631	0	70	64	33	83	15	91
239	17	98	60	8	95	4	98
357	16	108	62	12	91	9	94
436	19	154	57	9	94	8	95

* Lime was added before secondary clarification of trickling filter effluent.

TABLE C2

A COMPARISON OF TRICKLING FILTER - TERTIARY PERFORMANCE
WITH THE EXISTING WILLOW LAKE STP FINAL EFFLUENT⁽¹⁾

TRICKLING- FILTER INFLUENT	CHEMICAL DOSES		LIME-RECARBONATED EFFLUENT mg/l ⁽³⁾			MIXED MEDIA FILTER EFFLUENT PSF MEDIA			CORRESPONDING VALUES ⁽⁴⁾ FINAL EFFLUENT WILLOW LAKE STP	
BOD mg/l	CaO mg/l	Mg mg/l	BOD	TSS	Org SS	BOD mg/l	TSS mg/l	Org SS mg/l	BOD mg/l	TSS mg/l
85-140	321-437	0	MODERATE CANNING - NO CORN - 85% SECONDARY BOD REMOVAL			4-6	1-6	1-2	18-24	38-42
186-340	397-631 ⁽²⁾	0	MODERATE CANNING - WITH CORN - 85% SECONDARY BOD REMOVAL			17-28	15-18	4-7	41-53	52-53
390-570	239-436	16-19	HEAVY CANNING - WITH CORN - 73% SECONDARY BOD REMOVAL			64-83 ⁽⁵⁾	5-9	2-9	108-160	41-71
280-390	379-423	16-19	MODERATE CANNING - WITH CORN - 69% SECONDARY BOD REMOVAL			-	-	-	70-125	52-79

(1) Existing discharge standard of 11,000 lbs. BOD/Day and 7,300 lbs. SS/Day requires a BOD of 41 mg/l and a suspended solids of 27 mg/l at 32.5 mgd.

(2) Result of BOD removal by Trickling Filter and not High Lime Dose.

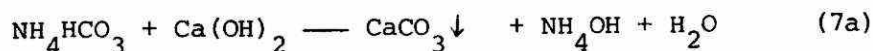
(3) 8-9 hr. composite 8 AM to 6 PM (Lime added to Trickling Filter Effluent).

(4) 24 hr. composite.

(5) Estimated from COD.

Cl.5 Nitrogen Removal

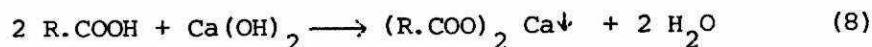
Nitrogen has been repeatedly implicated as a nutrient which can be as important as phosphorus in the eutrophication of a body of water. Equations 7a and 7b indicate that in an alkaline environment, one is able to convert ammonium salts to gaseous (and volatile) ammonia.



Thus, the removal of ammonia from the water can be achieved at elevated pH's and by passing large quantities of air through the liquid. Such a process, which shall be described more fully elsewhere is referred to as ammonium air stripping.

Cl.6 Organic Acid Neutralization

Organic acids reacting with calcium hydroxide may form salts which upon crystallization will precipitate.



Little appears to have been published on this mechanism, but it could account for some of the BOD_5 reduction observed in lime treated raw wastewater.

Thus, by the addition of lime, at least eight separate reactions take place as the pH is increased, resulting in a cleaner effluent. Lime treatment has the advantage, as compared with other coagulants, of reducing the total hardness (or total salts) of the effluent, which may be quite important if it is to be immediately reused. The interdependency of these reactions will be reviewed in more detail later.

Cl.7 Heavy Metal Removal

The precipitation of metal hydroxides is dependent upon the concentration of the metal ion in solution and the pH of the solution.

Equation 9 indicates the interdependency of pH, metal concentration, and metal solubility; as pH increases the solubility of the metal hydroxide ($Mx(OH)_2$) decreases,

$$\frac{[Mx^{++}][OH^-]^2}{[Mx(OH)_2]} = K_{sp} \text{ (solubility product)} \quad (9)$$

Table C3, taken from Argo et al (88), lists the solubility products of heavy metal hydroxides.

TABLE C3 SOLUBILITY PRODUCTS OF CATIONIC HEAVY METAL OXIDES OR HYDROXIDES

<u>Compound</u>	<u>K_{sp}</u>
SnO	1×10^{-61}
Au(OH) ₃	8.5×10^{-45}
Ti(OH) ₃	1×10^{-40}
Fe(OH) ₃	6×10^{-38}
Cr(OH) ₃	1×10^{-30}
HgO	3×10^{-26}
Cu(OH) ₂	3×10^{-19}
Zn	4.5×10^{-17}
Fe(OH) ₂	1.8×10^{-15}
Pb ₂ O(OH) ₂	1.6×10^{-15}
Cd(OH) ₂	2×10^{-14}
Mn(OH)	2×10^{-13}
BiOOH	3×10^{-11}
BaSO ₄	1×10^{-10}
BaCO ₃	1.6×10^{-9}
Ag ₂ O	2×10^{-8}

In most cases, pH adjustment to 11.5 will remove the offending heavy metals, and, in some instances, to a level below the predicted value, presumably by adsorption on chemical floc.

Table C4 (88) reveals the amount of heavy metals present before and after lime treatment of domestic and industrial effluents.

TABLE C4

LIME COAGULATION AND RECARBONATION

Metal	Ref.	Concentration Before Treatment mg/l	Concentration After Treatment mg/l	Final pH	Percent Removal
Antimony ¹	5			11	~90
Arsenic ¹	5			11	<10
Barium ¹	5		~ 1.3(sol) ²	11	
Bismuth ¹	5		0.0002(sol)	11	
Cadmium	14	Trace		11	~ 50
	15	0.0137	0.00075	>11	94.5
Chromium (+6)	15	0.056	0.050	>11	11
Chromium (+3)	16	7.400	2.7	8.7	99.9+
Copper	16	15.700	0.79	8.7	99.9+
	17	7	1	8	86
	17	7	0.05	9.5	93
	18	302	Trace	9.1	99+
Gold ¹	5		<.001(sol)	11	90+
Iron	18	13	2.4	9.1	82
	19	17	0.1	10.8	99+
	19	2.0	1.2 ³	10.5	40
Lead ¹	5		<.0001(sol)	11	90+
Manganese	19	2.3	<0.1	10.8	96
	19	2.0	1.1 ³	10.5	45
	20	21.0	0.05	9.5	95
Mercury ¹	5		Oxide soluble		<10
Molybdenum	14	Trace		8.2	~ 10
Nickel	16	160	0.08	8.7	99.9+
	17	5	0.5	8	90
	17	5	0.5	9.5	90
	21	100	1.5	10.0	99
Selenium	15	0.0123	0.0103	>11	16.2
Silver	15	0.0546	0.0164	>11	97
Tellurium ¹ 4	5		(<0.001?)	11	(?90+)
Titanium ¹ 4	5		(<0.001?)	11	(?90+)
Uranium ⁵	5 ²		?		?
Zinc	5		.007(sol)	11	90+

See Notes on next page.

NOTES FOR TABLE C4

1. The potential removal of these metals was estimated from solubility data.
2. Barium and lead reductions and solubilities are based upon the carbonate.
3. These data were from experiments using iron and manganese in the organic form.
4. Titanium and Tellurium solubility and stability data made the potential reduction estimates unsure.
5. Uranium forms complexes with carbonate ion. Quantitative data were unavailable to allow determination of this effect.
6. Temperature: Ambient 20-25°C.

Lindstedt et al (55) adjusted wastewaters to approximately pH 11, and measured heavy metal removal using isotopes. They found Ag, Cd, Se, Cr were decreased by 97, 94.5, 16.2 and 9.3 per cent, respectively.

Because of the increasing stringency of regulations dealing with heavy metal discharges to receiving waters (Table C5), it appears the lime treatment will be used for economical removal of these elements.

TABLE C5 REGULATORY AGENCY REQUIREMENTS

Constituents in the injection water not to exceed the following concentrations:

Constituent	Concentration (mg/l except electrical conductivity and pH)
Electrical Conductivity	900 μ mhos/cm
pH	6.5 to 8.0
Ammonium	1.0
Sodium	110
Total Hardness (as CaCO_3)	220
Sulfate	125
Chloride	120
Total Nitrogen (as N)	10
Fluoride	0.8
Boron	0.5
MBAS	0.5
Hexavalent Chromium	0.05
Cadmium	0.01
Selenium	0.01
Phenol	0.001
Copper	1.0
Lead	0.05
Mercury	0.005
Arsenic	0.05
Iron	0.3
Manganese	0.05
Barium	1.0
Silver	0.05
Cyanide	0.2

The Injection water shall not cause taste, odours, foam or colour in ground water.

The filter effluent turbidity shall not exceed 1.0 unit.

The carbon adsorption column effluent shall not exceed a chemical oxygen demand concentration of 30 mg/l.

The chlorine contact basin effluent shall always contain a free chlorine residual.

C2 LOW pH TREATMENT OF WASTEWATER

Low pH treatment of wastewater usually is a moderate lime addition to pH 9.5 or 10.0. Such a system can precede a biological system, or may be part of an entirely physical-chemical system, or may be used as tertiary treatment on a conventional system.

C2.1 Chemical-Biological-Anaerobic Digestion

The system proposed and successfully operated by Black and Lewandowski (2) is an example of a chemical-biological system (Figure C5). The raw sewage, treated with lime to pH 9.3 undergoes primary clarification by a lime sludge which settles out carrying down with it 82% of the total phosphorus (2, 52). The lime treated effluent is brought to an activated sludge unit, where the CO₂ liberated from microbial metabolism serves to reduce the pH from 9.3 to a biologically amenable value of 7.8. The lime sludge can be anaerobically digested along with the conventional sludge. Presumably, the anaerobic digester must be emptied more frequently with the introduction of lime sludge.

The same authors (2) indicate that by adding lime prior to rather than after the aerators, they were able to reduce the BOD and SS going to the aerators by 72% and 78% respectively. They noted a supplemental beneficial effect of lime: "The lime addition improved phosphorus removal within the primary clarifier, but also resulted in an effluent much lower in organic solids, reducing appreciably the organic load on the secondary process."

In 1967, Buzzell et al (4) had found that a lime treatment alone to pH 11.0 could effect an 80% to 90% removal of phosphorus, 97% removal of suspended solids, a 50% to 70% reduction in BOD, a 25% removal of nitrogen and a 99.9% destruction of coliforms. However, they had limited success with a subsequent activated sludge process, because, in their opinion, the effluent from the lime treatment was too weak for proper functioning of the biological system.

C2.2 Chemical-Biological Incineration

Schmid and McKinney (7) had proposed a related system similar to those just described; however, they advocated sludge incineration rather than anaerobic digestion. They observed a decrease in suspended

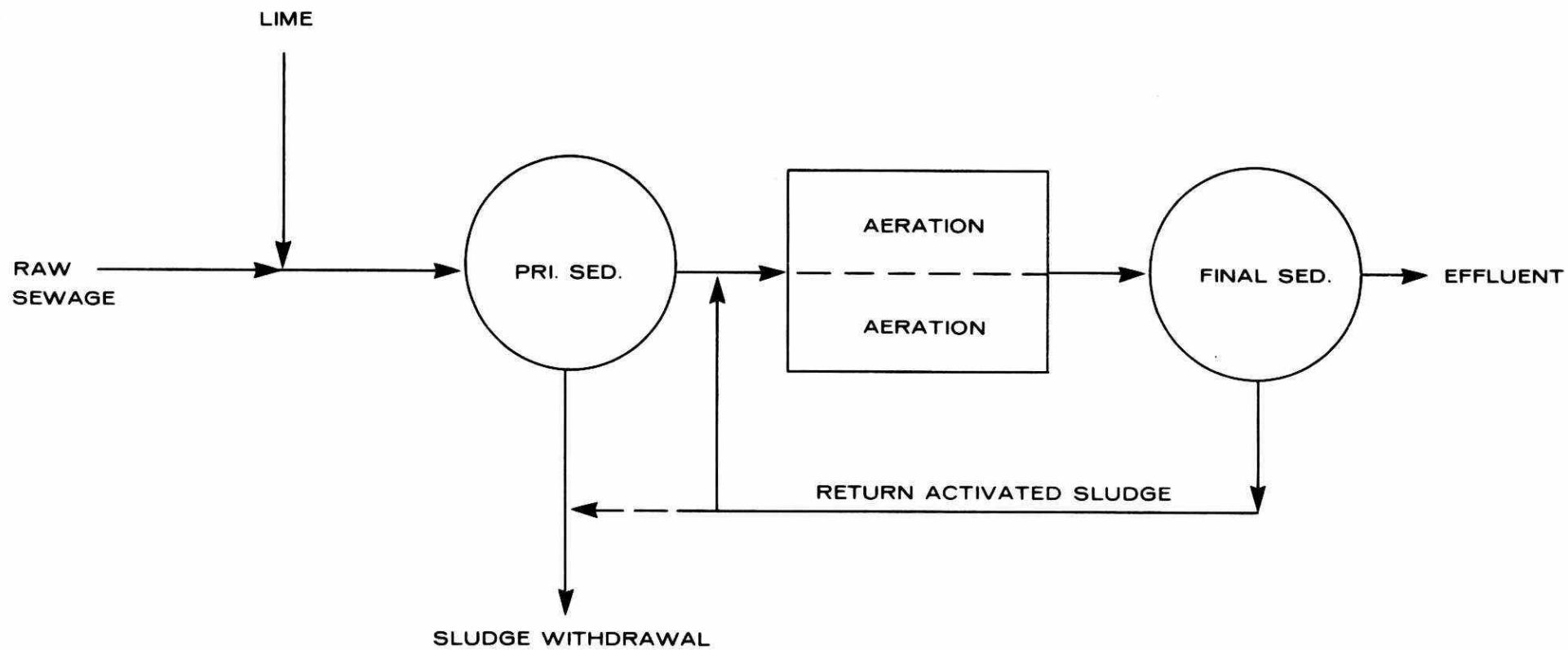


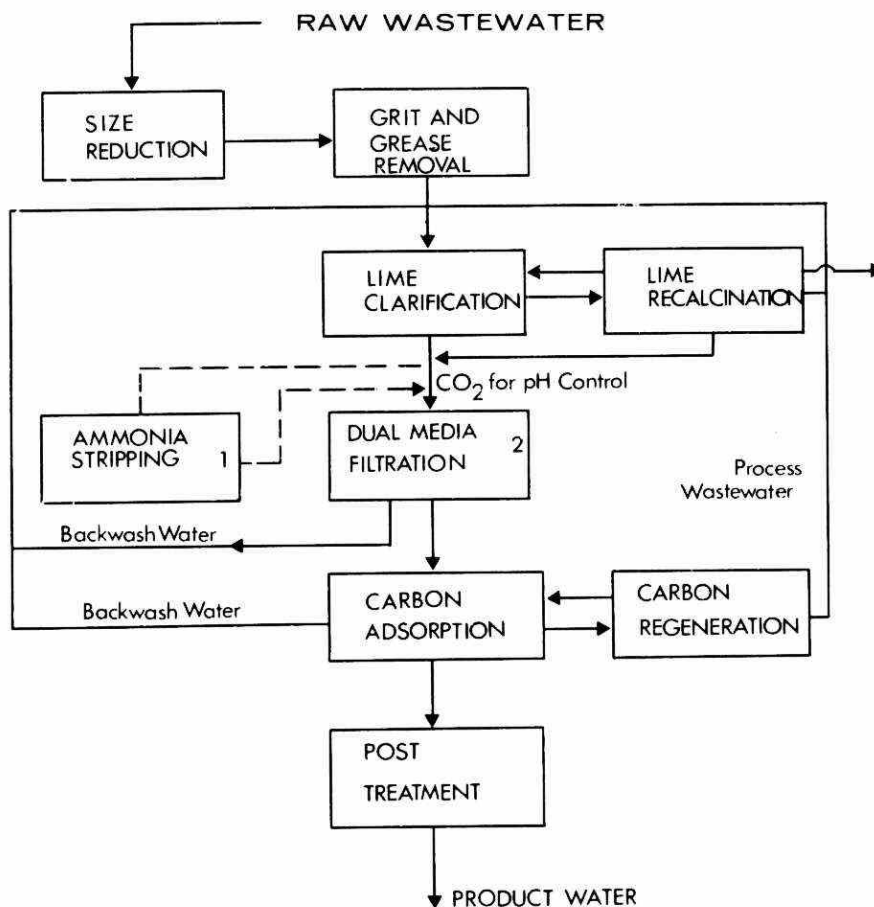
Figure C5 Chemical-Biological System Proposed By Black Et Al. (2)

solids, chemical oxygen demand (COD) and phosphate (PO_4) from 312, 670 and 38 mg/l respectively to values of 45, 295, and 7.1 when the pH was adjusted to 9.4.

C2.3 Chemical-Biological Recalcination

Villiers et al (15) proposed a pH adjustment to 9.5 followed by dual media filtration and carbon adsorption with the feasibility of having ammonia stripping, lime recalcination regeneration as shown in Figure C6. The carbonation step should follow ammonia stripping, and not vice-versa as shown in Figure C6.

Figure C6 Schematic Diagram of Proposed Wastewater Treatment System.



- (1) IF NITROGEN REMOVAL IS REQUIRED
- (2) COULD BE REPLACED BY FILTRATION IN THE CARBON CONTACTORS
- (3) CHLORINATION, OZONATION, ETC.

Table C6 shows the design parameters of the described system:

TABLE C6 DESIGN PARAMETERS FOR MUNICIPAL WASTEWATER
TREATMENT PLANTS USING LIME CLARIFICATION
AND CARBON ADSORPTION

<u>Lime clarification process</u>	
Clarifier	
Rise rate	1 gpm/ft ² to
Range of variation	5 gpm/ft ²
Operation	Upflow
Operation pH	9.5
Lime dosage	250 mg/l
Range of variation	150-350 mg/l
Dual media filtration	
Surface loading	2 gpm/ft ²
Range of variation	5 gpm/ft ²
<u>Carbon adsorption process</u>	
Operation	Downflow
Operation pH	7.5
Surface loading	7 gpm/ft ²
Range of variation	14 gpm/ft ²
Carbon particle size	8 x 30 mesh
Residence time, empty bed	50 min

The initial lime treatment improved the water quality to such an extent (Table C7) that the burden on the subsequent carbon contact was eased considerably.

An effluent of such quality is certainly equal to that obtained from only the best operated conventional wastewater treatment systems. Furthermore, one of the major advantages of such a system is that it is possible to remove the sludge during the calcination process. However, Villiers et al (15) do not propose any alternative methods for sludge disposal since calcination may not always be economically feasible in physical treatment systems, especially in small municipalities.

TABLE C7

EFFECT OF LIME TREATMENT

	<u>TOC</u>	<u>BOD</u>	<u>COD</u>	<u>SS</u>	<u>P</u>	<u>JTU</u>
Raw Sewage	79	76	192	109	9	54
Lime Clarification	36 (45)	39 (49)	84 (56)	30 (72)	0.3 (97)	11
Dual Media Filtration	27 (25)	23 (41)	61 (27)	10 (66)	0.3 (0)	2
Granular Carbon Adsorption	10 (63)	11 (52)	27 (44)	1 (90)	0.3 (0)	1
<p>TOC: Total Organic carbon</p> <p>BOD: Biochemical oxygen demand</p> <p>COD: Chemical oxygen demand</p> <p>SS: Suspended solids</p> <p>P: Phosphorus</p> <p>JTU: Jackson turbidity units</p> <p>(): Figures in parenthesis represent per cent decrease in value from preceding value - all data in mg/l except turbidity.</p>						

The same authors (15) indicated three major shortcomings in the conventional system and credit the physical-chemical system with three bonuses:

Conventional System:

1. The operation and control of a conventional system is complex.
2. The system is easily upset and may require considerable time to re-establish normal operation.
3. The problem of sludge disposal.

Physical-Chemical System:

1. It is less complex and operates on easily measurable parameters.
2. The process can be turned off and/or rapidly adjusted to changing conditions.
3. The operation is predictable and therefore amenable to instrumentation and automation.

In their comparison of conventional with physical-chemical treatment systems, they included an estimate of relative costs. As can be seen from Tables C8 and C9 there appears to be no significant cost difference.

TABLE C8 ESTIMATED CAPITAL AND OPERATING COSTS FOR
1, 10 AND 100 MGD LIME CLARIFICATION AND
CARBON ADSORPTION MUNICIPAL WASTEWATER

	<u>1 mgd</u>	<u>10 mgd</u>	<u>100 mgd</u>
<u>Lime clarification process</u>			
Capital costs, \$	400,000	1,600,000	7,160,000
Amortization of capital,			
¢/1000 gal	8.6	3.4	1.6
Operating and maintenance			
cost, ¢/1000 gal	15.3	6.5	3.5
Total treatment cost			
¢/1000 gal	23.9	9.9	5.1
<u>Carbon adsorption process</u>			
Capital costs, \$	400,000	1,700,000	12,190,000
Amortization of capital,			
¢/1000 gal	8.6	3.6	2.6
Operating and maintenance			
¢/1000 gal	23.7	7.2	4.6
Total treatment cost			
¢/1000 gal	32.3	10.8	7.2
<u>Total treatment system</u>			
Capital costs, \$	800,000	3,300,000	19,350,000
Amortization of capital,			
¢/1000 gal	17.2	7.0	4.2
Operating and maintenance			
cost ¢/1000 gal	39.0	13.7	8.1
Total treatment cost			
¢/1000 gal	56.2	20.7	12.3

TABLE C9 ESTIMATED CAPITAL COSTS FOR A 10 MGD CONVENTIONAL
 ACTIVATED SLUDGE TREATMENT PLANT WITH SLUDGE DISPOSAL
 BY THICKENING, FILTRATION AND
 INCINERATION (1)

Capital costs, \$	3,950,000
Operating costs ¢/1000 gal	
Primary treatment	4.0
Secondary treatment	3.0
Sludge disposal	4.5
Amortization of capital, (2)	
¢/1000	8.5
<hr/> Total costs, <hr/>	20.0

(1) Jan. 1970 dollars

(2) 6% over 25 years

C2.4 Kinetics of Phosphorus Removal at Low and High pH

Ferguson et al (10, 12) critically examined the interdependency of pH, time, and seed on the degree and rate of phosphorus removal. Below pH 9, it was found that the CaCO_3 did not readily precipitate and the reduction of phosphate as calcium phosphate took place over many hours. See Figure C7.

At pH 10 and 11, there was a very rapid precipitation of calcium phosphate. It was also noted that increased carbonate content of wastewater reduced the rate of phosphorus removal. It was thought that the carbonate affected the nucleation and crystal growth of calcium phosphate.

The same authors also examined the effect of magnesium on the rate of phosphorus removal. At pH 8.0, the presence of magnesium retarded the rate of phosphorus removal presumably by altering calcium hydroxy apatite crystal growth through competition of the magnesium for a site on the crystal lattice. At pH 9.5 they found a definite improvement in phosphorus removal with the addition of magnesium because both the calcium carbonate and calcium phosphate are able to precipitate at this pH.

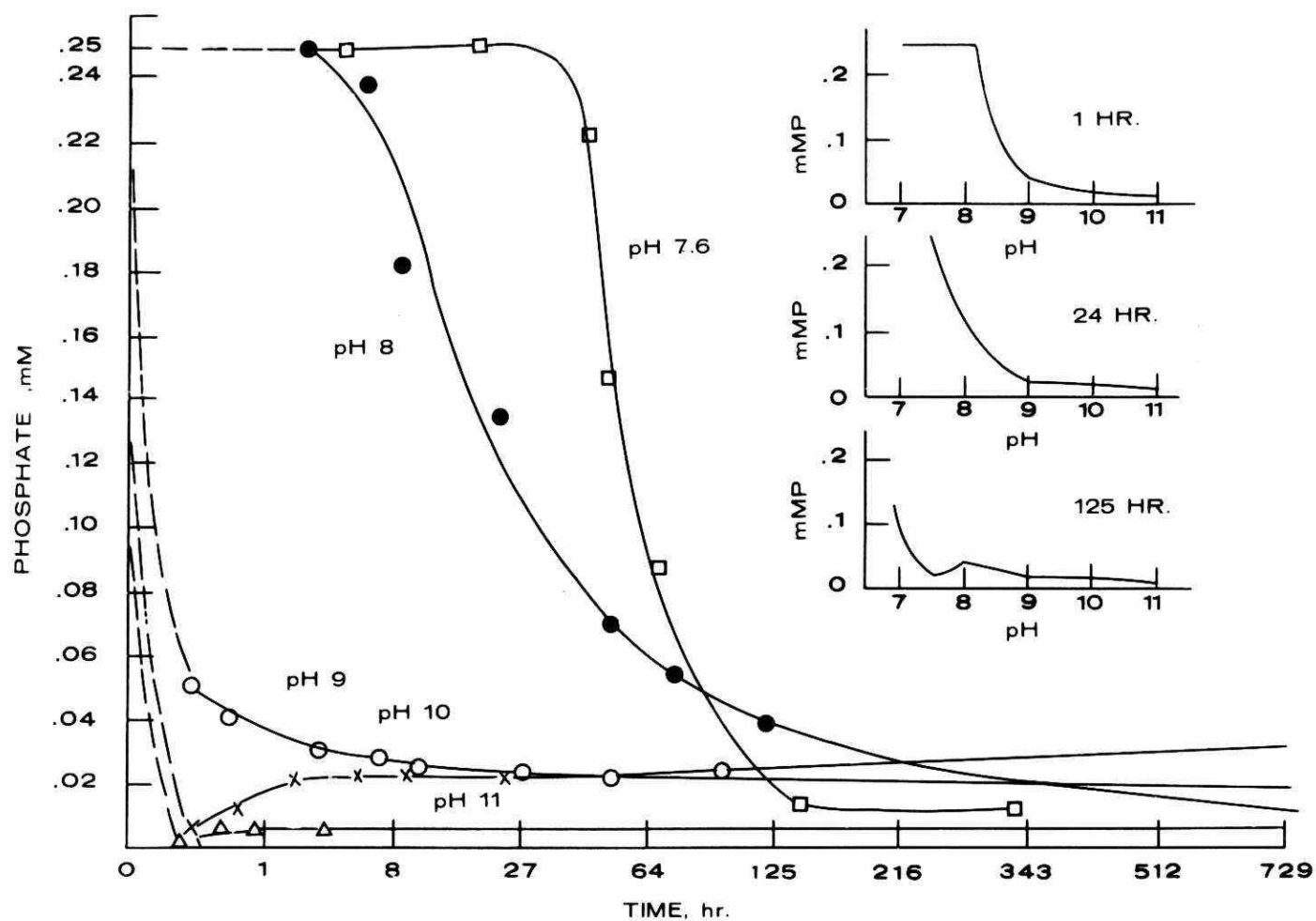


Figure C7 The Effect of pH and Time On Phosphate Removal. Initial Conditions: $\text{CO}_3\text{t} = 0.0038 \text{ M}$, $\text{Ca}_\text{t} = 0.0020 \text{ M}$, $\text{PO}_4\text{t} = 0.00025 \text{ M}$, $T = 26 \pm 1^\circ\text{C}$.

C3 HIGH pH TREATMENT OF WASTEWATER

A number of U.S.A. municipalities, e.g. Washington (Blue Plains) (18), Lebanon (19) and Lake Tahoe (14) have investigated or are using high pH as one of several stages in a treatment system for the removal of phosphorus as well as air stripping of ammonia. The Lebanon single-stage precipitation system reduced the total phosphorus to less than 0.5 mg/l phosphorus by adjusting the pH to 9.5 - 10.0. Lake Tahoe and Washington used a two stage precipitation and sedimentation system of pH 11 to 12 with intermediate carbonation.

O'Farrell et al (18) found that treating secondary effluents with lime to pH 11.5 permitted sedimentation at overflow rates of 1500 gal/sq ft/day. The effluent was subsequently carbonated, settled, and filtered to give a final effluent in which there was less than 0.30 mg/l of total phosphorus and a TOC of less than 15 mg/l.

Stamberg (20) attributes excellent phosphorus removal to the formation and flocculation of magnesium hydroxide at a pH of 11.5 or higher which aids in precipitation, especially of the particulate organics. The calcium carbonate increases floc density thereby permitting high overflow rates. Stamberg also indicated that below pH 11.5 the total phosphorus (dissolved and unsettlable) usually exceeded 2 mg/l out of the clarifier unless a flocculant such as ferric hydroxide was added. The turbidity and phosphorus found below pH 11.5 (without flocculants) was not easily or effectively removed by dual media filtration.

C3.1 Interdependency of Calcium, Magnesium, and Phosphorus

In effluents with elevated phosphorus levels, the carbonate may not precipitate readily at pH levels of ten or lower. It appears that the phosphorus is adsorbed on the growth faces of the calcium carbonate nuclei thereby preventing further crystal growth and thus inhibiting the precipitation of the calcium carbonate (20). The lime sludge that formed at pH levels of ten or lower appeared gelatinous and had poor settling characteristics. As the pH increased above ten, the settling and dewatering properties improved (20).

At pH 11.5, Stamberg (20) found that in all Washington, D.C. wastewaters he examined, magnesium was required as a flocculant to clarify

the water and to improve phosphorus removal. He indicated that five to ten mg/l of magnesium ion is sufficient to produce good clarification and that the magnesium is essentially completely precipitated between pH 11.5 and 11.8. Under these conditions, the treated effluent contained approximately 0.3 mg/l of phosphorus and the TOC was reduced from 100 to 20 mg/l.

C3.2 Dissolved Calcium and pH

It was observed that the total residual calcium (unsettleable particulate and soluble) increased only very slightly with lime additions to pH 10. Apparently the calcium from the lime precipitates the phosphates and carbonates from the water and they are settled out rapidly (equations 2 and 3). Beyond pH 10, the residual calcium decreased even though lime was being added and there was essentially no phosphate remaining to precipitate. This decrease in calcium was attributed to the precipitation of the bicarbonate alkalinity as calcium carbonate. At pH 11.5, the bicarbonate alkalinity was totally removed, hence the addition of lime proportionally increased the residual calcium ion content in the supernatant.

C3.3 Clarification of Treated Effluents

In moderately alkaline wastewaters (100 to 150 mg/l as CaCO_3), such as those found in Washington (18), the entire precipitation of the bicarbonate alkalinity was required to permit a high overflow rate and low turbidity. On the other hand, wastewaters of high alkalinity (350 mg/l as CaCO_3) (19) formed sufficient calcium carbonate between pH 9.5 to 10 to produce sludge with satisfactory calcium carbonate characteristics. However, the authors reported considerable haze caused by calcium and phosphate suspended precipitates up to pH 11.5. At, and beyond, pH 11.5 the haze was eliminated.

Measurements of the magnesium, calcium and phosphorus ion revealed that efficient clarification and phosphorus removals at pH 11.5 or greater occurred as magnesium was precipitated as magnesium hydroxide (Figure C8).

It was concluded that magnesium hydroxide was the necessary flocculant to clarify the water and to improve phosphorus removal.

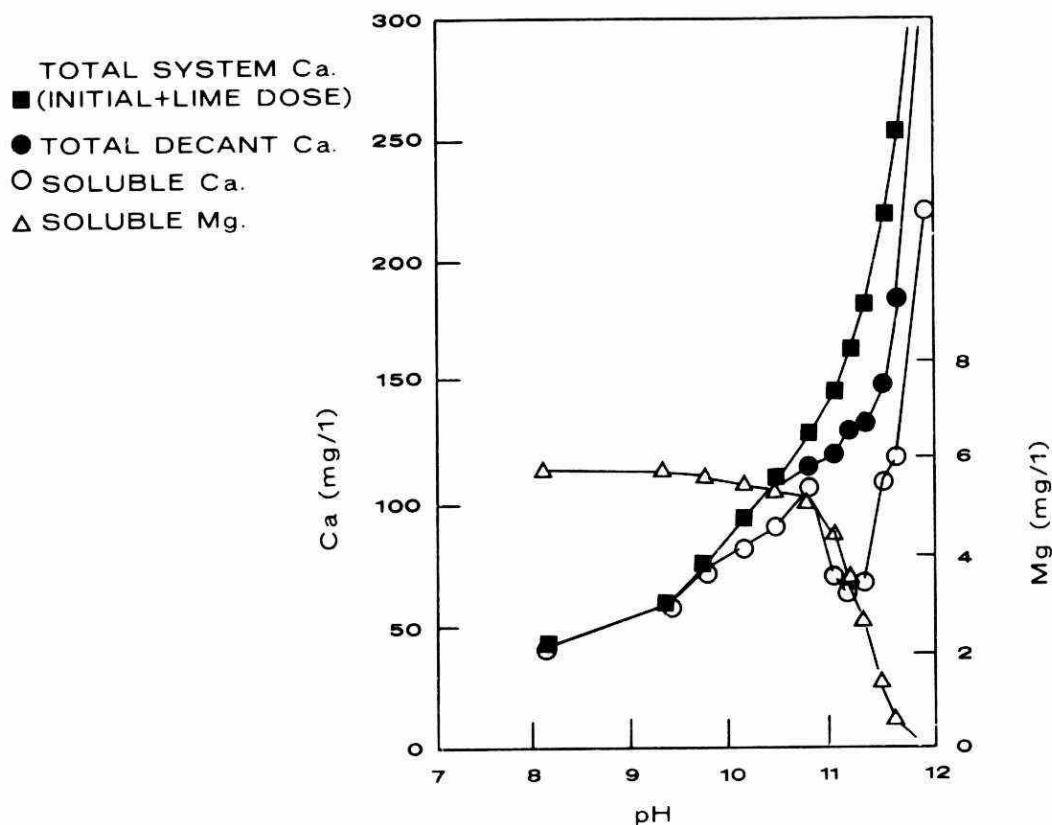


Figure C8 Calcium and Magnesium Concentrations During a Metaphosphate Removal.

Phosphorus which is not present as a simple phosphate is removed by a mechanism other than calcium hydroxyapatite precipitation. The meta, tripoly, and pyrophosphates are removed by adsorption on freshly precipitated calcium carbonate and magnesium hydroxide, or by alkaline hydrolysis to orthophosphate and subsequent precipitation to apatite. The organically bound phosphorus is removed with the suspended solids, especially at a pH above 11.5 where magnesium hydroxide is precipitated and coagulates particulate organics (20). In the Washington effluent, 5 - 10 mg/l of magnesium ions was sufficient to produce a clear effluent.

C3.4 pH Adjustment in Nitrified Effluents

Nitrified effluents are the easiest to adjust to pH 11.5. In the conversion of ammonia to nitrate, nitric acid is formed which is neutralized by the bicarbonate system.



According to the above reaction, 14 mg/l of NH_4^+ will convert 100 mg/l bicarbonate alkalinity (as CaCO_3) to carbonic acid. Stamberg et al (20) report that 60 mg/l of lime is required to adjust the nitrified effluent to a pH of 11.5.

The removal of dissolved and particulate organic material is also readily achieved with lime. Typical results noted (20) were a reduction in TOC from 100 to 20 mg/l, and a residual turbidity of less than two JTU units, less than one JTU unit if magnesium was used.

Stamberg's study (20) suggested a treatment system with: primary sedimentation; secondary treatment with nitrification; lime precipitation with filtration for solids separation; and finally carbon adsorption which, at the same time, also causes biological denitrification.

C4.1 Carbonation of Treated Effluents

Because of the elevated pH of the lime treated effluents, it is necessary to reduce the pH to levels that will not alter the condition of the receiving waters or cause calcium scaling or upset the bicarbonate equilibrium.

The most commonly used method for pH adjustment is by treatment with carbon dioxide, although methods using sulphuric acid (15) and sodium carbonate (18) have been suggested.

Carbonation can be carried out in either one or two stages depending on whether or not the effluent is to undergo further treatment after carbonation. In a single stage system, the pH is reduced from its high value to approximately pH 7.0 in one step. Should the pH be reduced too rapidly, most of the calcium will remain in solution resulting in unnecessarily hard waters and, if the sludge is calcined, there will also be a loss of valuable calcium carbonate. The other disadvantage of a single stage carbonation system to pH 7 is the minimum solubility of calcium carbonate at pH 9.3 as explained below.

In the two stage carbonation, the primary carbonation reduces the elevated pH to pH 9.3, at which calcium carbonate is least soluble. This results in the maximum amount of calcium being precipitated from solution as a large, heavy, and rapidly settling floc. If sufficient time is provided for the reaction to go to completion (approximately 15 minutes), the floc will not redissolve with subsequent lowering of the pH which should theoretically increase the solubility of calcium carbonate (44).

Work by the Continental Can Co. at Hodge, Louisiana, however, has shown that carbonating to a pH below 9.3 will solubilize the fine CaCO_3 precipitate in suspension thereby eliminating any haze (personal communication). Usually, the second stage in carbonation involves adjusting the pH to 7. This pH is preferred because it increases the efficiency of organic removal by carbon columns, prevents scaling of filters or carbon particles, and prevents scaling in receiving waters.

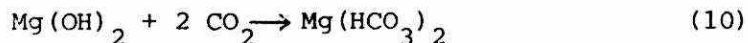
It has also been stressed that 8.8 is the highest tolerable pH, otherwise extensive calcium carbonate deposits will form on the filters and carbon system. However, each carbonation system should be experimented with to determine the optimal and most economical operation.

Tofflemire working with low alkalinity waters (30) found that with a single stage carbonation from pH's 10.8 to 8.7 without the use of settling tanks to remove the calcium carbonate, there was no build up of calcium carbonate on the carbon columns. Without carbonation when working at pH 9.6, some calcium carbonate was deposited on the columns but this could easily be removed by back washings. The effluent which he examined was an almost equal mixture of municipal and paper mill effluents giving a combined alkalinity of 150 mg/l as calcium carbonate.

C4.2 Carbonation of Lime Sludges

Thompson et al (41) were the first to suggest the recovery of magnesium from the lime sludge. The system is elegantly simple and presumably will be put into use providing carbonation costs do not exceed the value of the magnesium recovered.

Carbonation of the sludge selectively solubilizes the magnesium by converting it from magnesium hydroxide to magnesium bicarbonate (equation 10). The remainder of the sludge is removed by vacuum filtration and the filtrate can be recycled as a coagulant, or may be further treated in order to crystalize out the magnesium carbonate trihydrate.

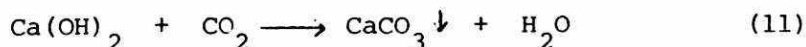


C4.3 Carbon Dioxide Requirements

If calcining or incinerating facilities exist on the site, this would appear to be the ideal source of carbon dioxide. Other sources include engine exhausts from various sources around the plant which may burn fuel oil, kerosene, propane, etc. Liquid carbon dioxide is the most convenient system, though transportation costs often make it financially unattractive.

The amount of carbon dioxide required to neutralize an effluent can be calculated from its hydroxyl and carbonate alkalinities at the

elevated pH (equation 11).



Since minor quantities of CaCO_3 remain in the effluent after removal of CaCO_3 in the clarifier, only small quantities of CO_2 are required to convert the carbonate ion to the bicarbonate form (equation 12).



The conversion of the CaCO_3 to $\text{Ca(HCO}_3)_2$ has the added advantage of significantly, if not totally, removing any haze present in the effluent.

Culp et al (44) provide a sample calculation where the water to be carbonated has a pH of 11.7, the hydroxide and carbonate alkalinities are 380 and 120 mg/l as CaCO_3 respectively, the gas contains 10% CO_2 at a temperature of 100°F and there is a built-in 20% error factor. (These conditions and requirements are quite similar to those of Lake Tahoe). Such a system required 3,256 lb CO_2 per million gallons of effluent or 270 cfm/mgd.

O'Farrell (18) required 280 mg/l and 86 mg/l for a two stage carbonation system (from pH 11.9 to 10.1 and 10.1 to 7.5, respectively). He did not state the alkalinities at pH 11.5 but the influent alkalinity was 152 mg/l as CaCO_3 . This carbon dioxide requirement of 3,052 lb/10⁶ gal is very similar to that indicated by Culp et al (44).

C4.4 Clarifier Size

Culp et al (44) recommend a 15 minute period for carbonation reaction to occur and another 15 minutes for the calcium carbonate to precipitate. Overflow rates of 2,400 gal/ft² per day should provide good clarification.

O'Farrell's (18) system is somewhat different in that he suggests a 170 rpm turbine mixer for 15 minutes followed by flocculation at 22 rpm in two extended flocculating basins in series, each with a 24 minute retention system.

C5 AMMONIA REMOVAL

There are a number of methods for the removal of nitrogen from wastewaters: microbial denitrification; selective ion exchange; electrolytic oxidation; adsorption on natural zeolites (e.g. clinoptilolite); breakpoint chlorination; ligand exchange; and air stripping. The method most suitable for lime treated wastewaters is either adsorption on clinoptilolite or air stripping.

C5.1 Natural Zeolites

Clinoptilolite (a natural rock which is crushed to approximately 30 mesh for use in packed columns) removes ammonium ions (NH_4^+) by releasing (exchanging) sodium or calcium ions. The columns can be regenerated repeatedly by washing with a lime-sodium chloride solution at pH 11. The effluent from the regeneration cycle can then be air stripped to remove the ammonia or it can be saved to react with the magnesium bicarbonate and calcium phosphate reclaimed from the lime sludge to produce magnesium ammonium phosphate.

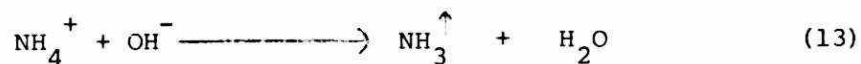
Cassel et al (68) operated a clinoptilolite ion exchange pilot plant for five months on lime clarified and filtered raw waste. They reported an average of 75% ammonia removal with 3.0 mg/l ammonium nitrogen being discharged. Apparently the removal efficiency could have been significantly increased had there been more manpower to properly operate the system. Mercer (69) obtained 95% ammonium nitrogen removal in a well-operated system. Cost estimates of 9.7 cents per 1000 gallons include the lime-sodium chloride regeneration, air stripping, sulphuric acid scrubbing of ammonia laden air. Clinoptilolite was estimated at 18 cents per lb.

C5.2 Air Stripping

Air stripping is presently the most popular non-biological method for removal of ammonium nitrogen and since up to 90% of nitrogen in raw wastewaters is ammonia or urea, it is a simple and inexpensive method for the removal of most of the total Kjeldhal nitrogen from wastes (44, 13).

Lime treated effluents are ideally suited for ammonia stripping, especially when treated with lime to pH's of 11 to 12. As the pH increases above neutrality, the equilibrium in the following reaction (equation 13)

is driven to the right, forcing the conversion of ammonium to the volatile ammonia.



In order to liberate the gas, the surface tension of the water must be reduced. This is usually accomplished by droplet formation or aerosol formation (44, 70). Large volumes of air are necessary for droplet formation and sweeping away the volatilized ammonia. As an added benefit in the air stripping of ammonia, the hydrogen ion released in the oxidation of ammonium to ammonia serves to reduce the pH of the effluent. This in turn reduces the carbonation requirements.

Albertson et al (17) indicated that at pH's of 10.5 to 11.0, approximately 500 cu ft of air were required per gallon of effluent to achieve removals of ammonia nitrogen of 90% to 95%.

Culp et al (44) reported that Kuhn, using a 7 ft tower packed with Raschig rings, was able to remove 92% of the ammonium nitrogen at pH 11 using 550 ft³ air/gal.

Slechta et al (13) used a 25' x 6' x 4' tower with redwood slats as baffles. They found a 90% reduction of ammonia-nitrogen at pH 11.5 with an air requirement of only 280 ft³ per gallon. The same authors found that temperature decreases from 17°C to 3°C reduced the ammonia stripping efficiency from 90% to 65%. Based on their study, a cost of \$8/million gallons was estimated for ammonia stripping in a 3.75 mgd plant amortized at 5% for 25 years. The ammonia stripping method has two limitations:

- 1) it cannot operate below freezing,
- 2) calcium carbonate scale deposits can markedly reduce the efficiency of the system.

The latter problem may be overcome with improved design. The temperature problem is unresolved at the moment, and the general consensus is that nitrogen could be discharged to the receiving waters in winter when biological (and mainly algal) activity is extremely reduced.

As previously mentioned, the handling and disposing of any sludge is a major problem and inconvenience in the treatment of wastewaters. Since lime treatment increases the amount of sludge produced, it was often rejected solely on the basis of sludge handling. However, recent investigations indicate a number of methods are available for simple and economical handling of these sludges.

C6.1 Land Disposal

The land disposal method is especially attractive for towns in rural areas where the organically enriched lime could be used as a fertilizer. This is especially attractive in areas where the soil is acidic. The broadcasting of regular biological sludges on farm lands has been practiced for a number of years in Europe (78), where considerable work has been undertaken to determine which method of sludge treatment will ensure a product free of harmful parasites, parasite eggs, bacteria and viruses. Sludge is considered to be of sufficient agricultural value to investigate heat treatment to render the sludge benign by pasteurization (78, 85, 86).

In North America, sewage sludge is not a popular product with the agrarian sector, and its acceptance has often been slow or non-existent, with a few exceptions (73, 75, 87). When sludge is land disposed, the prime reason has been to get rid of it, rather than use it as a land beneficator.

Guidelines have been established by various regulating bodies, such as the Ontario Ministry of the Environment (81), in an attempt to prevent spread of disease through broadcasting of untreated sludges. However, the present standard appears to be somewhat too general: i.e. "sludge which has undergone proper anaerobic or aerobic digestion or other suitable processing at a municipal sewage treatment plant".

C6.1.1 Public Health Aspects

A paper presented by Humble et al at the 1972 American Society of Microbiology, and the work of Hoover (59), Doyle (62), Dotson (75), Farrell (76), Tullander (60), Richl (63) Buzzell et al (21) indicates quite clearly that high pH treatment of wastewaters produces effluents

practically free of microorganisms. Doyle suggested that all undigested sludges should be adjusted to pH 12 with lime to ensure a safer and more odour-free product for disposal. Such a sludge would also be practically free of pathogenic organisms and could thereby be broadcast without fear.

Work in progress in the U.S.A. (53, 65) indicates that high pH and lime coagulation may be the most effective method for the elimination of disease causing viruses. Since chlorination has little effect on viruses, lime treatment may be an effective way to remove and inactivate the agents responsible for hepatitis, jaundice, polio, etc. Berg et al (65) have shown increased polio disinfection with increased pH. Lund (64), on the other hand, indicates that at high pH viruses are not removed from the water but are only slightly inactivated. His findings indicate that some viruses are still active in the sludge and consequently extra caution may be required in land disposal of sludges. Evidently more research is required in this area. A research group in San Antonio, Texas, is presently exploring the use of lime for viral inactivation. Their results should provide guidelines and definite answers on the safety of land disposal of lime sludges, vis-a-vis viral contamination. However, it is expected that prolonged exposure to high pH and elevated salt concentrations will cause protein denaturation and will probably render the host receptor site recognition mechanism inoperative. The work of Berg et al (65) clearly showed that the addition of lime to pH 11.5 would rapidly destroy polio virus I. They found:

100%	survival	after	120	minutes	exposure	to	pH	10.1
40%	"	"	"	"	"	"	"	pH 10.8
<1%	"	"	"	"	"	"	"	pH 11.1

At such a rate of decrease with increasing pH, if extrapolated to pH 11.5, there would be no survivors.

Investigations by Manwaring (56) using ferric chloride (FeCl_3) and Chadhuri (66) using ferric sulfate and alum as flocculants for virus removal found that although the viruses were effectively removed from the wastewaters, they remained virulent in the sludge. The authors warned against the possible health hazards in land disposal of such sludges.

Further work is certainly required to determine if surface and ground waters do become virally contaminated through such practices.

It appears then that lime will become a widely used chemical in the treatment of wastewaters, based on its ability to disinfect bacteria, parasites, parasite eggs and viruses. Should certain disease producing organisms survive in a high pH sludge, then heat pasteurization, incineration or recalcination might be required. This would be especially true during epidemics.

The use of high pH rather than chlorination for bacterial destruction appears even more probable because of the extremely toxic chloramines produced by chlorination in conventional waste treatment facilities (83, 90).

C6.1.2 Heavy Metals

Land disposal of sludges may introduce heavy metals into the soil. This is especially true with lime sludges since the high pH treatment will cause most metals in the wastes to precipitate as the metal oxides or hydroxides (88). However, because of the low concentration of heavy metals in the effluents on non-industrial towns, their low solubility of alkaline pH, and the fact that they are tightly bound in the soil, it appears that heavy metal contamination from sludges may not be a serious problem, as previously believed (61). The evidence put forth by Latham (89) concerning Milorganite indicates that heavy metal contamination in land disposal of biologically digested sludges is not a problem even with sludge from an industrialized city such as Milwaukee. Considerable work has already been carried out and further work is in progress, both in Canada and the U.S.A. to determine the extent and rate of heavy metals leaching into groundwaters and/or their translocation through plants. Professor Bates of the University of Guelph, in Guelph, Ontario, is actively involved in this type of research (91).

Considerable research involving all phases of interaction between man and heavy metals is being conducted throughout the scientific world. Inevitably new information concerning the feasibility of lime sludge disposal will be forthcoming. Symposia such as those conducted at the University of Missouri (84) are invaluable in the transmission and propagation of this research.

C6.2 Chemical Recovery of Sludges

In large wastewater treatment plants, considerable quantities of lime sludge are produced daily. Recalcination offers the best solution in such plants. In so doing, the organics are burned and the calcium carbonate is converted to calcium oxide. The carbon dioxide given off in the process may be used in the carbonation of the high pH effluent to an acceptable pH level.

According to the hardness of the water being treated, it may or may not be necessary to add make-up calcium oxide. In hard waters, and at high pH treatment, more calcium will be precipitated as calcium carbonate than will remain in solution, even though considerable lime may be required to raise the pH to the desired level. With increased cycles of the calcined lime, there is a corresponding increase of insoluble contaminants such as calcium hydroxyapatite and ash. It may be possible to recover the phosphorus for use in the manufacture of phosphoric acid, or of triple superphosphate, or of magnesium ammonium phosphate, a slow release fertilizer obtained by reaction of the phosphorus with magnesium (also present in the sludge or magnesium hydroxide) and with ammonium (also available in wastewaters) (22). The work of Salutsky et al (57) is a fairly detailed study of various methods for the extraction of magnesium ammonium phosphate from wastewaters.

The investigations of DuBose and Black (58) have suggested a novel approach to magnesium ammonium phosphate recovery in a high pH lime treatment system for wastewaters. The lime sludge formed from treatment at pH 11.5 is carbonated to approximately pH 9, which converts the magnesium hydroxide to soluble magnesium bicarbonate trihydrate.

The mother liquor, rich in the magnesium bicarbonate, can be reacted under proper conditions with the digester supernatant liquor collected from an existing conventional treatment system. This concept of waste treatment would effectively remove phosphorus from lime-treated effluents and would provide an inexpensive source of magnesium for removing the phosphorus and ammonia from digester supernatants.

If magnesium hydroxide is used in the lime process as a coagulant aid, then the magnesium can be reclaimed from the sludge as magnesium

bicarbonate trihydrate by carbonation to pH 9 with carbon dioxide from the calciner. The magnesium bicarbonate trihydroxide is added back to the beginning of the system and recycled in this fashion. Depending on the hardness of the water, there may be a net surplus of magnesium.

C7 LIME SLUDGE HANDLING PROCESSES

C7.1 Clarification

The method of clarification of lime treated wastewater appears dependent on the treatment method employed. Normally, treatment consists of a rapid flash mixing of chemicals, flocculation, and sedimentation. Where a portion of the sludge from the clarifier is recycled back to the clarifier, the degree of removal and the rate of precipitation is improved, but the system may suffer from increased upsets. Moreover, there is a definite decrease in pH with sludge recycling which necessitates increased lime dosages to achieve the same pH attained without sludge recycle. However, Albertson et al (17) reported that recirculation of the sludge increased COD reductions as great as 50%, i.e. an equivalent phosphorus removal was obtained at a lower pH. They used sludge from the clarifier underflow to maintain suspended solids of 500 to 2000 mg/l. O'Farrell (18) also recommended 10% solids recycle into the internal reaction zone of the first-stage chemical clarifier (an upflow-flocculator-clarifier with side walls 12 ft deep; and a turbine mixer at 30 rpm for 40 minutes).

Single stage clarification is preferred with a low pH (9.5) treatment which does not require carbonation. In high pH systems, where carbonation is necessary, there is a definite advantage in two stage clarification. Overflow rates are usually quite high. Tofflemire (30) for example, used a clarifier overflow rate of 400 gpd/sq ft with a retention time of two hours and a 5 gpm flow rate. He found that the addition of 0.5 mg/l of anionic polymers had slight beneficial effects at low overflow rates. However, at high overflow rates (twice that without polymers) the polymers permitted good solids removal. Among those tested, he reported that four were particularly effective.

R 1583-130B	(National Starch & Chemical)
Deolyte 930	(Diamond Shamrock Crop.)
Atlasep 2A2	(Atlas Chemical Ind.)
Dow A-23	(Dow Chemicals Co.)

Albertson et al (17) found that with a sludge recycle they could operate the clarifier at overflow rates of 2000 gpd/sq ft.

Ferric ions also have been successfully used as a flocculant aid in solids (calcium carbonate) removal of carbonated effluents (18).

C7.2 Sludge Dewatering

Three methods are commonly used for dewatering sludges:

- 1) Drying beds,
- 2) Vacuum filtration,
- 3) Centrifuging.

Because of the rapid settling and the non-gelatinous nature of the heavy calcium carbonates and other calcium and magnesium salts, lime sludges are well suited to dry bedding. Furthermore, these sludges are odour-free (62) and attract no flies or other vermin (personal communication-A.P. Black). Within a day, solid levels of 20% to 25% are frequently attained (30). A counter-current centrifugal system is used at Lake Tahoe (44) for dewatering. This type of system usually operates best on a solids feed of approximately 10%, thereby necessitating lime mud thickeners to precede centrifugation. The resultant sludge cake emitted from the centrifuge is 50% - 55% solids. At Lake Tahoe, the phosphorus is separated from the calcium solids since the bulk of the calcium is in the cake and the phosphorus is discharged in the centrate. Classification of solids in such a fashion is an ideal method of preventing the build-up of phosphorus and inert materials in the recalcination stage.

Filtration appears to be a sound method for solids removal, and may become the preferred method for dewatering of lime sludges. Work at Welwyn Hall (32) indicates that the addition of anionic polyelectrolytes to lime treated sludges improved the floc strength appreciably, thereby considerably increasing filtrability.

The work of DuBose and Black (58) indicates that magnesium hydroxide gives tenacity and strength to the lime sludges thereby significantly increasing its dewaterability either in dry beds or by vacuum filtration. However, Nelson (26) is uncertain as to whether magnesium hydroxide governs the settling rate, sludge volume, or dewaterability, but has some evidence that carbonation improved thickening and centri-

fugation of lime sludge.

A detailed survey of thickeners, centrifuges, and vacuum filters is available and should be consulted for more ample information (72).

C7.3 Sludge Calcination

The decision to calcine the sludge in order to regenerate calcium oxide and burn off the organic material is primarily a financial one. If this decision is being considered, there are a number of questions that remain to be answered:

1. How active is the new product?
2. Will the recovered lime affect the removal efficiencies?
3. How serious is the phosphorus, magnesium, and inert build up during repeated recycling?
4. Is re-used lime as easy to dewater and filter - i.e. sludge specific resistance?
5. Is slaking affected in re-used lime?
6. What are the most appropriate calcining conditions to ensure complete oxidation without excessive clinkers and dead-burns?
7. Should a multiple hearth furnace or a fluidized bed be used in the calcination?

Since the performance of a calcination system is very much dependent upon the local water conditions and because of the limited scope of this review, the reader is referred to Mulbarger et al (23), Culp and Culp (44), and Parson (67) for detailed examinations of these problems.

The lime dosage required to raise the pH to a given value will vary considerably from one waste to another. The amount of lime will be related to the alkalinity, the bicarbonate concentration, the CO_2 , the calcium and magnesium concentrations, the type and quantity of phosphorus (phosphate buffer), the amount of ammonia (ammonia-ammonium buffer), the type and quantity of organics, the degree of biological treatment, the temperature and the ionic strength (20).

Table C10 is a summary of the data on the amount of lime required to increase the pH of various effluents to specific levels. As shown in the table, there is considerable latitude in the results, and the amount of lime required must be determined individually for each effluent. Figures C9 and C10 serve as a good guideline for lime requirements in wastewater of known alkalinity.

Buzzell et al (4) developed a rough guideline in which they indicated that the amount of lime (in mg/l) needed to reach pH 11 was approximately two to two and a half times the alkalinity value expressed in mg/l CaCO_3 . Stamberg's data shows that this rule of thumb may not always hold. Thompson et al (42) suggest the following mathematical approach for the determination of the lime requirements for high pH treatment and coagulation of the magnesium for potable water treatment. Presumably, minor modifications would make it appropriate for use in wastewater systems.

<u>Reaction</u>	<u>Lime required, mg/l of Ca(OH)_2</u>
$\text{CO}_2 + \text{Ca(OH)}_2$	$\text{CO}_2 \times \frac{\text{Ca(OH)}_2}{\text{CO}_2} \quad \frac{74}{100} =$
$2(\text{HCO}_3^-) + \text{Ca(OH)}_2$	$\text{Alk (as CaCO}_3) \times \frac{\text{Ca(OH)}_2}{\text{CaCO}_3} \quad \frac{74}{100} =$
$\text{MgCO}_3 \cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2$	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \times \frac{\text{Ca(OH)}_2}{\text{MgCO}_3 \cdot 3\text{H}_2\text{O}} \quad \frac{74}{100} =$
$\text{Mg}^{++} + \text{Ca(OH)}_2$	$\text{Mg}^{++} (\text{CaCO}_3) \times \frac{\text{Ca(OH)}_2}{\text{CaCO}_3} \quad \frac{74}{100} =$

TABLE C10

pH, ALKALINITY, AND LIME DOSE RELATIONSHIPS

Alkalinity mg/l as CaCO ₃	pH	CaO mg/l	Ca(OH) ₂ mg/l	Reference No.
381	10	315		2
-	9.5		250	15
-	11.5		393	55
142	11.5	300		18
152	11.9	460		18
-	11.5	400		13
120	10.0	130		20
22	11.0	64		20
120	11.0	168		20
240	11.0	244		20
600	11.0	390		20
400	11.0	450		23
-	8.5	69		28
231	10.0	225		30
-	11.0	545		6
-	11.4		300	36
-	9.5-10		200	17

Since 90% pure CaO is usually slaked, the total lime dosage found above would be multiplied by -

$$\frac{100}{90} \times \frac{56}{74}, \text{ i.e. } 0.82$$

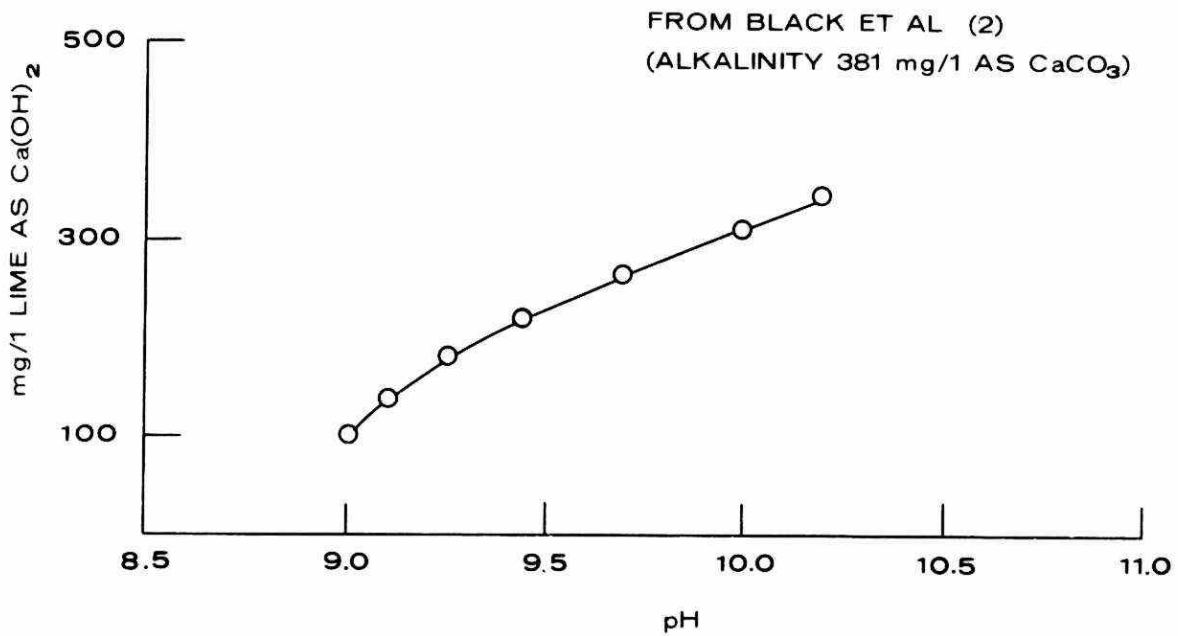


Figure C9 pH As a Function of Lime Dose and Alkalinity.

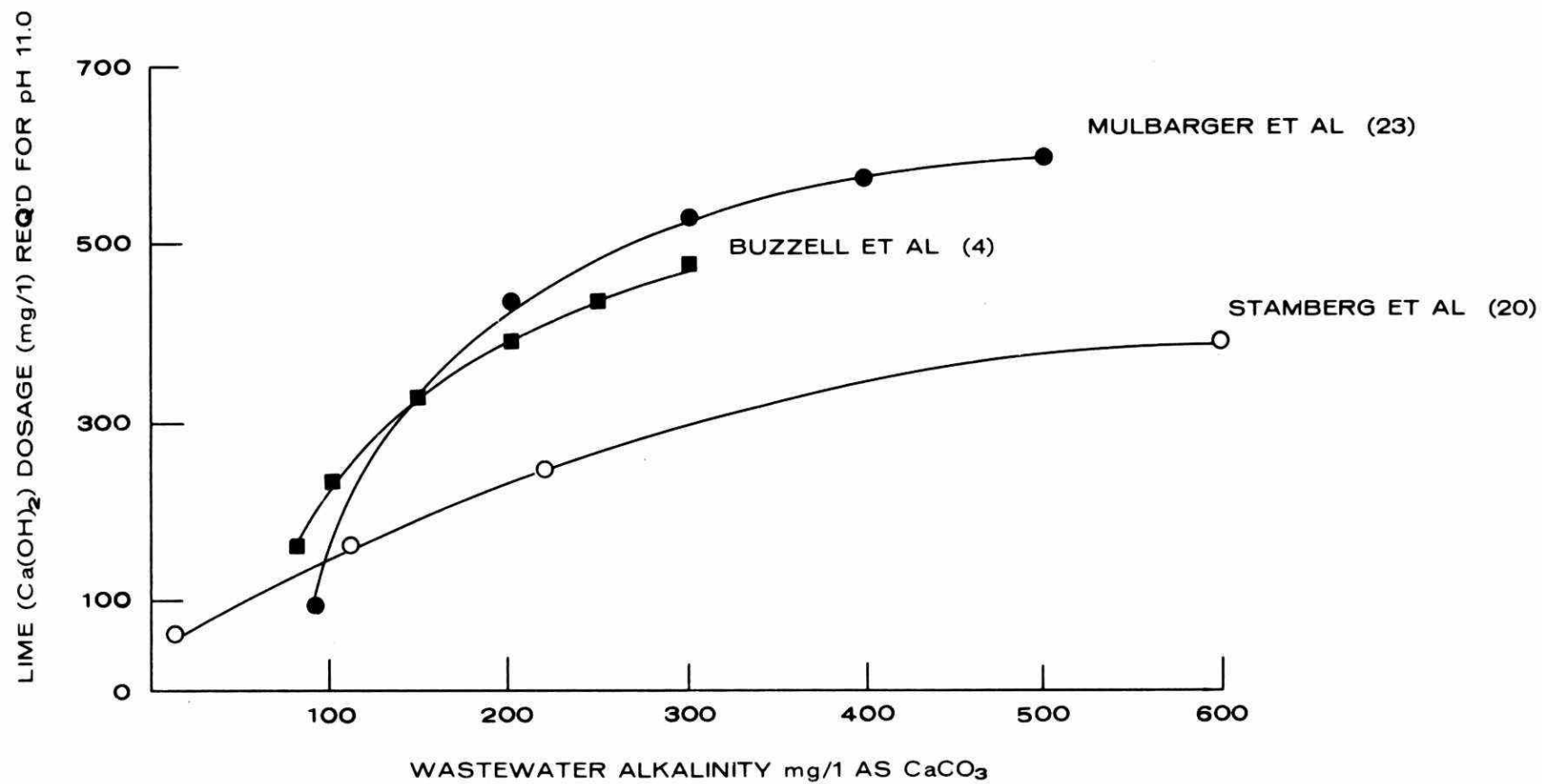


Figure C10 Lime Dose Required For pH 11.0 In Wastewater of Various Alkalinity.

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